

Encyclopedia of Materials:
COMPOSITES

Editor in Chief
Dermot Brabazon

Section Editors

Manoj Gupta

Fatima Zivic

Eva Pellicer

Robertt Valente

Mohamed El Mansori

Lorna Fitzsimons

Antonello Astarita



ENCYCLOPEDIA OF MATERIALS: COMPOSITES

Volume 1

ENCYCLOPEDIA OF MATERIALS: COMPOSITES

EDITOR IN CHIEF

Dermot Brabazon

*I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology
Research Centre, School of Mechanical and Manufacturing Engineering,
Dublin City University, Dublin, Ireland*

Volume 1

Section Editors

Section 1: *Metal Matrix Composite Materials*, Edited by Manoj Gupta

Section 2: *Polymer Matrix Composite Materials*, Edited by Dermot Brabazon



AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge MA 02139, United States

Copyright © 2021 Elsevier Inc. All rights reserved

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers may always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-12-819724-0

For information on all publications visit our
website at <http://store.elsevier.com>



Publisher: Oliver Walter
Acquisitions Editor: Ruth Rhodes and Kelsey Connors
Content Project Manager: Laura Jackson
Associate Content Project Manager: Sajana Devasi
Designer: Mark Rogers

CONTENTS OF VOLUME 1

Contents of Volume 1	v
List of Contributors for Volume 1	xi
Editorial Board	xvii
Preface	xix

VOLUME 1

Section 1: Metal Matrix Composite Materials, Edited by Manoj Gupta

Introduction to Metal Matrix Composite Materials: An Introduction <i>Manoj Gupta</i>	1
Fundamentals of Metal Matrix Composites <i>Sankaranarayanan Seetharaman and Manoj Gupta</i>	11
An Insight Into Metal Matrix Composites With Micron Size Reinforcement <i>Arsha Antony Geetha, Madhusoodhanan Geethakumari Akhil, Thazhivilai Ponnu Devaraj Rajan, and Ballambettu Chandrasekhara Pai</i>	30
An Insight Into Metal Matrix Composites With Nano Size Reinforcement <i>Massoud Malaki</i>	42
An Insight Into Magnesium Based Metal Matrix Composites With Hybrid Reinforcement <i>Sankaranarayanan Seetharaman, Subramanian Jayalakshmi, Ramachandra Arvind Singh, and Manoj Gupta</i>	52
Metal Based Composites With Metastable/Amorphous Reinforcements <i>Penchal Reddy Matli and Manoj Gupta</i>	78
Development and Properties of Amorphous Particles Reinforced Al Matrix Nanocomposites <i>Adnan Khan, Mattli M Reddy, Penchal Reddy Matli, Rana A Shakoor, and Manoj Gupta</i>	96
Metal Matrix Syntactic Composites <i>Vyasraj Manakari, Gururaj Parande, Manoj Gupta, and Mrityunjay Doddamani</i>	109
Insight Into Layered Metal Matrix Composites <i>Akshay Padnuru Sripathy and Manoj Gupta</i>	121
Eco-friendly Metal Matrix Composites <i>Gururaj Parande, Vyasraj Manakari, and Manoj Gupta</i>	140
Liquid Phase Processing of Metal Matrix Composites <i>Madhusoodhanan Geethakumari Akhil, Kaimanikal Madhurananthan Nair Sree Manu, Thazhivilai Ponnu Devaraj Rajan, and Ballambettu Chandrasekhara Pai</i>	160
Solid Phase Processing of Metal Matrix Composites <i>Mingyang Zhou, Lingbao Ren, Gaofeng Quan, and Manoj Gupta</i>	173
Two Phase Processing of Metal Matrix Composites <i>Penchal Reddy Matli, Tirumalai Srivatsan, and Manoj Gupta</i>	197

Additive Manufacturing of Metal Matrix Composites <i>Sankaranarayanan Seetharaman and Manoj Gupta</i>	209
Severe Plastic Deformation Processing of Metal Matrix Composites <i>Sankaranarayanan Seetharaman, Ankita Mandal, and Manoj Gupta</i>	230
Friction Stir Processing of Metal Matrix Composites <i>VK Bupesh Raja and Manoj Gupta</i>	247
An Insight Into Processing Maps of Metal Matrix Composites <i>Biranchi N Sahoo and Sushanta K Panigrahi</i>	257
Microstructural Aspects of Metal-Matrix Composites <i>Devadas Bhat Panemangalore and Rajashekhara Shabadi</i>	274
Tensile Characteristics of Metal Matrix Composites <i>Milli S Kujur, Ved P Dubey, Ashis Mallick, and Manoj Gupta</i>	298
Tensile Response of Al-Based Nanocomposites <i>Penchal Reddy Matli, Vyasraj Manakari, Gururaj Parande, and Manoj Gupta</i>	313
Compressive Response of Aluminum Metal Matrix Composites <i>Ramanathan Arunachalam and Pradeep K Krishnan</i>	325
Fatigue Behavior of Magnesium Matrix Composites <i>Sravya Tekumalla and Manoj Gupta</i>	344
High-Temperature Properties of Metal Matrix Composites <i>Oluseyi P Oladijo, Samuel A Awe, Esther T Akinlabi, Resego R Phiri, Lebudi L Colliueus, and Rebaone E Phuti</i>	360
Creep Characteristics of Metal Matrix Composites <i>Hong Yang, Sarkis Gavras, and Hajo Dieringa</i>	375
Tribological Properties of Light Metal Matrix Composites <i>Jitendra K Katiyar, Jaafar Al Hammad, and Abdul Samad Mohammed</i>	389
Mechanical and Tribological Properties of Aluminum Based Metal Matrix Nanocomposites <i>Mir Ifan Ul Haq, Sanjay Mohan, Ankush Raina, Subramanian Jayalakshmi, Ramachandra Arvind Singh, Xizhang Chen, Sergey Konovalov, and Manoj Gupta</i>	402
Damping Characteristics of Metal Matrix Composites <i>Penchal Reddy Matli and Manoj Gupta</i>	415
Electromagnetic Shielding Capabilities of Metal Matrix Composites <i>Anisha Chaudhary, Vinay Gupta, Satish Teotia, Subhash Nimanpure, and Dipen K Rajak</i>	428
Corrosion Characteristics of Metal Matrix Composites <i>Devadas Bhat Panemangalore and Udaya Bhat K</i>	442
Coating Technologies for Metal Matrix Composites <i>Sumit Pramanik and Kamal K Kar</i>	454
Biocompatibility of Metal Matrix Composites Used for Biomedical Applications <i>Somasundaram Prasadh, Santhosh Suresh, Vaishnavi Ratheesh, Raymond Wong, and Manoj Gupta</i>	474
Joining of Metal Matrix Composites <i>VK Bupesh Raja and Manoj Gupta</i>	502
High Performance Machining of Metal Matrix Composites <i>Keng S Woon</i>	512
Application of Metal Matrix Composites in Engineering Sectors <i>Dipen K Rajak and Pradeep L Menezes</i>	525

Metal Matrix Composites for Automotive Components in Depth Case Study: Development of Automotive Brake Disc <i>Nanang Fatchurrohman and Shamsuddin Sulaiman</i>	540
--	-----

Application of Metal Matrix Composites in Non-Structural Applications <i>Mubarak Ali M, Mohamed Thariq, Vishwesh Dikshit, and Bhudolia S Kumar</i>	557
---	-----

Section 2: Polymer Matrix Composite Materials, Edited by Dermot Brabazon

Introduction: Polymer Matrix Composite Materials <i>Dermot Brabazon</i>	563
--	-----

Particulate Reinforced Polymer Matrix Composites

Overview of Mechanical and Physicochemical Properties of Polymer Matrix Composites <i>Kai Bin Liew, Choon Fu Goh, Sajid Asghar, and Haroon K Syed</i>	565
--	-----

Processing of Polymers and Their Composites: A Review <i>Jaspreet Singh, Kulwinder Singh, JS Saini, and Mohammed SJ Hashmi</i>	577
---	-----

Tailored Behavior of Polymer Matrix Composite Materials <i>Yousef Tamsilian, Samira Alvani, Fatemeh Abdolkhani, and Elham Khademi Moghadam</i>	604
---	-----

Effect of Particle Size and Content of Crumb Rubber on the Dynamic Properties of Passenger Tyre Tread Using Finite Element Method <i>Adnan A Alshukri, Faieza A Aziz, Mohd S Salit, Nuraini A Aziz, and Mohammed Al-Maamori</i>	615
--	-----

Overview of Surface Roughness Effect on Silver Nanoparticle Filled Epoxy Composites <i>MA Salim, R Hamidi, and AM Saad</i>	628
---	-----

Polymer Single-Screw Extrusion With Metal Powder Reinforcement <i>Rupinder Singh, N Singh, P Bedi, and IPS Ahuja</i>	671
---	-----

Polymer Twin Screw Extrusion With Filler Powder Reinforcement <i>Rupinder Singh, Sunpreet Singh, and Mohammed SJ Hashmi</i>	691
--	-----

The Effect of In-Situ-Formed Silver Nanoparticles on the Morphological Properties of Epoxy Resin Filled Composites <i>MA Salim, R Hamidi, and AM Saad</i>	706
--	-----

Toughening Mechanisms of Devulcanized Rubber Modified Epoxy Based Composites Reinforced With Zirconia <i>Alaeddin B Irez, Emin Bayraktar, and Ibrahim Miskioglu</i>	713
--	-----

Polymer Nanocomposite Characterization and Applications <i>Mahsa Shirazi, Gholamreza Masoudi Rad, and Yousef Tamsilian</i>	725
---	-----

Fibre Reinforced Polymer Matrix Composites

Effect of Fiber Orientation on the Mechanical Properties of Laminated Polymer Composites <i>N Ghamarian, Mohamed AA Hanim, P Penjumras, and Dayang LA Majid</i>	746
--	-----

Tensile Properties of Woven Intra-Ply Carbon/Kevlar Reinforced Epoxy Hybrid Composite at Sub-Ambient Temperature <i>Nurain Hashim, Dayang LA Majid, Danish M Baitab, Noorfaizal Yidris, and Rizal Zahari</i>	766
---	-----

Thermoplastic Composites for Fused Deposition Modeling Filament: Challenges and Applications <i>Kamaljit S Boparai and Rupinder Singh</i>	774
--	-----

Biomedical Applications of Polymer Matrix Composites

Hydroxyapatite Based Polymer Composites for Regenerative Medicine Applications <i>Luis J del Valle and Jordi Puiggali</i>	785
Biopolymer Matrix Composite for Drug Delivery Applications in Cancer <i>Ankit Jain, Madhavi Tripathi, Shiv K Prajapati, and Ashok M Raichur</i>	804
Covalent and Electrostatic Protein-Polysaccharide Systems for Encapsulation of Nutraceuticals <i>Hadis Rostamabadi, Seid Reza Falsafi, and Seid Mahdi Jafari</i>	818
Polymer Matrix Composites Containing Carbon Nanomaterials for Medical Applications <i>Maryam Ahmadzadeh Tofighy, Soha Habibi, and Toraj Mohammadi</i>	832
Biopolymer Matrix Composites for New Medical Applications <i>Zahra Shariatinia</i>	842
Poly(methyl methacrylate)-Based Composite Bone Cements With Different Types of Reinforcement Agents <i>Sanaz Soleymani Eil Bakhtiari, Hamid Reza Bakhsheshi-Rad, Saeed Karbasi, Ahmad Fauzi Ismail, Safian Sharif, Alexander Seifalian, Houman Savoji, and Filippo Berto</i>	867
Hydrogel Composite Films for Wound Healing <i>Ikram U Khan, Huma Mahmood, Yasser Shahzad, Sajid Asghar, and Haroon K Syed</i>	887
Polymer Composites for Organ Reconstruction <i>Haroon K Syed, Sajid Asghar, Kai Bin Liew, Ikram U Khan, Fizza A Razzaq, and Saba Rafique</i>	905
Overview of Additive Manufacturing Biopolymer Composites <i>Bankole I Oladapo, S Abolfazl Zahedi, Vincent A Balogun, Sikiru O Ismail, and Yarjan A Samad</i>	915
Marine Polysaccharide-Based Composite Hydrogels <i>Saad Salman, Syed H Khalid, Ikram U Khan, Sajid Asghar, Fahad H Shah, and Muniba Tariq</i>	929

Other Application Areas for Polymer Matrix Composites

Multifunctional Polymer Matrix Composites <i>Sajid Asghar, Haroon K Syed, Kai Bin Liew, Ikram U Khan, and Saad Salman</i>	937
Polymer Matrix Composite Materials for Aerospace Applications <i>Subramani Devaraju and Muthukaruppan Alagar</i>	947
Tribology of Polymer Matrix Composites Within the Automotive Industry <i>Leonardo I Farfan-Cabrera, Monica Tapia-Gaspar, and José Pérez-González</i>	970
Polymer Matrix Composites Materials for Water and Wastewater Treatment Applications <i>Maryam Ahmadzadeh Tofighy and Toraj Mohammadi</i>	983
Nanomaterial-Incorporated Polymer Composites for Industrial Effluent: From Synthesis to Application <i>Yousef Tamsilian, Mahsa Shirazi, and Gholamreza Masoudi Rad</i>	998

New and Emerging Processing Methods for Polymer Matrix Composites

Additive Manufacturing of Polymer Matrix Composites <i>Farnoosh Pahlevanzadeh, Hamid Reza Bakhsheshi-Rad, Dermot Brabazon, Mahshid Kharaziha, Ahmad Fauzi Ismail, Safian Sharif, Mahmood Razzaghi, and Filippo Berto</i>	1013
New Design Consideration of Polymer Matrix Composite Materials <i>Peng Liu</i>	1029

Thermal and Morphological Analyses of Polymer Matrix Composites <i>Subramani Devaraju, Arumugam Hariharan, Krishnasamy Balaji, and Muthukaruppan Alagar</i>	1038
A New Design of Epoxy Based Composites Reinforced With Devulcanized Rubber, Alumina Fiber and BN <i>Alaeddin B Irez, Emin Bayraktar, and Ibrahim Miskioglu</i>	1069
Development of Low-Cost Graphene-Polymer Blended In-House Filament for Fused Deposition Modeling <i>Rupinder Singh and Ranvijay Kumar</i>	1081
PLA Composite Matrix as Functional Prototypes for Four Dimensional Applications <i>Sudhir Kumar, Rupinder Singh, Tajinder P Singh, and Ajay Batish</i>	1091
Extrusion-Based Additive Manufacturing Techniques for Biomedical Applications <i>Ghazal Tadayyon, Daniel J Kelly, and Michael G Monaghan</i>	1101
Preparation and Applications of Synergically Combined Polymer Matrix Composites <i>Shashank T Mhaske and Arjit Gadgil</i>	1112

LIST OF CONTRIBUTORS FOR VOLUME 1

Fatemeh Abdolkhani
Shahid Chamran University of Ahvaz, Ahvaz, Iran

I.P.S. Ahuja
Punjabi University Patiala, Patiala, India

Madhusoodhanan Geethakumari Akhil
Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India and Academy of Scientific and Innovative Research, Ghaziabad, New Delhi, India

Esther T. Akinlabi
Pan African University for Life and Earth Sciences Institute, Ibadan, Nigeria

Mohammed Al-Maamori
University of Babylon-Iraq, Babylon, Iraq

Muthukaruppan Alagar
PSG Institute of Technology and Applied Research, Coimbatore, India

Mubarak Ali M
TKM College of Engineering, Kollam, Kerala, India

Adnan A. Alshukri
University Putra Malaysia, Serdang, Selangor, Malaysia and State Company for Rubber and Tyres Industry, Najaf, Iraq

Samira Alvani
Shahid Chamran University of Ahvaz, Ahvaz, Iran

Ramanathan Arunachalam
Sultan Qaboos University, Muscat, Oman

Sajid Asghar
Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Samuel A. Awe
Automotive Components Floby AB, Floby, Sweden

Faieza A. Aziz
University Putra Malaysia, Serdang, Selangor, Malaysia

Nuraini A. Aziz
University Putra Malaysia, Serdang, Selangor, Malaysia

Jaafar Al Hammad
King Fahd University of Petroleum and Minerals, Dhahran, Kingdom of Saudi Arabia

Mohamed A.A. Hanim
Universiti Putra Malaysia, Serdang, Selangor, Malaysia

Danish M. Baitab
University Putra Malaysia, Serdang, Selangor Darul Ehsan, Malaysia

Hamid Reza Bakhsheshi-Rad
Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran and Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Krishnasamy Balaji
PSG Institute of Technology and Applied Research, Coimbatore, India

Vincent A. Balogun
Edo University Iyamho, Iyamho, Edo State, Nigeria

Ajay Batish
Thapar Institute of Engineering and Technology, Patiala, India

Emin Bayraktar
Supmeca-Paris, School of Mechanical and Manufacturing Engineering, Saint-Ouen, France

P. Bedi
Guru Nanak Dev Engineering College, Ludhiana, India

Filippo Berto
Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway

Udaya Bhat K
Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar, Karnataka, India

Devadas Bhat Panemangalore
Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar, Karnataka, India

Kamaljit S. Boparai
MRS Punjab Technical University, Bathinda, India

Dermot Brabazon
I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin, Ireland

Anisha Chaudhary
University of Delhi, New Delhi, India

Xizhang Chen
Wenzhou University, Wenzhou, China

Lebudi L. Colliueus
*Botswana International University of Science and
Technology, Palapye, Botswana*

Luis J. del Valle
*Chemical Engineering Department, Polytechnic
University of Catalonia, Barcelona, Spain*

Subramani Devaraju
*Vignan's Foundation for Science, Technology and
Research, Guntur, India*

Hajo Dieringa
Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Vishwesh Dikshit
Nanyang Technological University, Singapore

Mrityunjay Doddamani
*National Institute of Technology Karnataka, Surathkal,
Karnataka, India*

Ved P. Dubey
*Indian Institute of Technology (Indian School of Mines)
Dhanbad, Dhanbad, India*

Seid Reza Falsafi
*Gorgan University of Agricultural Sciences and Natural
Resources, Gorgan, Iran*

Leonardo I. Farfan-Cabrera
*Tecnologico de Monterrey, Escuela de Ingeniería y
Ciencias, Monterrey, México*

Nanang Fatchurrohman
Universiti Malaysia Pahang, Pekan, Pahang, Malaysia

Ahmad Fauzi Ismail
*Advanced Membrane Technology Research Center
(AMTEC), Universiti Teknologi Malaysia, Johor Bahru,
Johor, Malaysia*

Arjit Gadgil
Institute of Chemical Technology, Mumbai, India

Sarkis Gavras
Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Arsha Antony Geetha
*Council of Scientific & Industrial Research–National
Institute for Interdisciplinary Science and Technology,
Trivandrum, Kerala, India and Academy of Scientific
and Innovative Research, Ghaziabad, New Delhi, India*

N. Ghamarian
Universiti Putra Malaysia, Serdang, Selangor, Malaysia

Choon Fu Goh
Universiti Sains Malaysia, Penang, Malaysia

Manoj Gupta
National University of Singapore, Singapore

Vinay Gupta
University of Delhi, New Delhi, India

Soha Habibi
Iran University of Science and Technology, Tehran, Iran

R. Hamidi
*Technical University of Malaysia Melaka, Durian
Tunggal, Melaka, Malaysia*

Arumugam Hariharan
*PSG Institute of Technology and Applied Research,
Coimbatore, India*

Nurain Hashim
*University Putra Malaysia, Serdang, Selangor Darul
Ehsan, Malaysia*

Mohammed S.J. Hashmi
Dublin City University, Dublin, Ireland

Alaeddin B. Irez
*CentraleSupélec, University Paris-Saclay, Gif-sur-Yvette,
France and University Paris-Saclay, Gif-sur-Yvette,
France*

Sikiru O. Ismail
University of Hertfordshire, Hatfield, United Kingdom

Seid Mahdi. Jafari
*Gorgan University of Agricultural Sciences and Natural
Resources, Gorgan, Iran*

Ankit Jain
Indian Institute of Science, Bangalore, Karnataka, India

Subramanian Jayalakshmi
Wenzhou University, Wenzhou, China

Kamal K. Kar
*Department of Mechanical Engineering and Materials
Science Programme, Indian Institute of Technology
Kanpur, Kanpur, India*

Saeed Karbasi
*Biomaterials and Tissue Engineering Department, School
of Advanced Technologies in Medicine, Isfahan
University of Medical Sciences, Isfahan, Iran*

Jitendra K. Katiyar
*SRM Institute of Science and Technology, Chennai,
Tamil Nadu, India*

Daniel J. Kelly
*Trinity College Dublin, Dublin, Ireland; Advance
Materials and BioEngineering Research(AMBER) Centre
at Trinity College Dublin and the Royal College of
Surgeons in Ireland, Dublin, Ireland; and Centre for*

Research in Medical Devices (CURAM), National University of Ireland, Galway, Ireland

Syed H. Khalid
Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Adnan Khan
Qatar University, Doha, Qatar

Ikram U. Khan
Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Mahshid Kharaziha
Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran

Sergey Konovalov
Samara National Research University, Samara, Russia

Pradeep K. Krishnan
National University of Science and Technology, Muscat, Oman

Milli S. Kujur
Indian Institute of Technology (Indian School of Mines) Dhanbad, Dhanbad, India

Bhudolia S. Kumar
Nanyang Technological University, Singapore

Ranjiv Kumar
Guru Nanak Dev Engineering College, Ludhiana, India

Sudhir Kumar
Thapar Institute of Engineering and Technology, Patiala, India

Kai Bin Liew
University of Cyberjaya, Cyberjaya, Selangor, Malaysia

Peng Liu
Lanzhou University, Lanzhou, China

Huma Mahmood
Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Dayang L.A. Majid
University Putra Malaysia, Serdang, Selangor Darul Ehsan, Malaysia

Massoud Malaki
Isfahan University of Technology, Isfahan, Iran

Ashis Mallick
Indian Institute of Technology (Indian School of Mines) Dhanbad, Dhanbad, India

Vyasraj Manakari
National University of Singapore, Singapore

Ankita Mandal
Indian Institute of Technology, Delhi, India

Kaimanikal Madhurananthan Nair Sree Manu
Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India and Brunel University, London, United Kingdom

Pradeep L. Menezes
University of Nevada, Reno, NV, United States

Shashank T. Mhaske
Institute of Chemical Technology, Mumbai, India

Ibrahim Miskioglu
Michigan Technological University ME-EM Department, Houghton, MI, United States

Elham Khademi Moghadam
Shahid Chamran University of Ahvaz, Ahvaz, Iran

Toraj Mohammadi
Iran University of Science and Technology, Tehran, Iran

Abdul Samad Mohammed
King Fahd University of Petroleum and Minerals, Dhahran, Kingdom of Saudi Arabia

Sanjay Mohan
Shri Mata Vaishno Devi University, Katra, Jammu, India

Michael G. Monaghan
Trinity College Dublin, Dublin, Ireland; Advance Materials and BioEngineering Research(AMBER) Centre at Trinity College Dublin and the Royal College of Surgeons in Ireland, Dublin, Ireland; and Centre for Research in Medical Devices (CURAM), National University of Ireland, Galway, Ireland

Subhash Nimanpure
Council of Scientific and Industrial Research, National Physical Laboratory, New Delhi, India

Bankole I. Oladapo
De Montfort University, Leicester, United Kingdom

Oluseyi P. Oladijo
Botswana International University of Science and Technology, Palapye, Botswana and University of Johannesburg, Johannesburg, Gauteng, South Africa

Akshay Padnuru Sripathy
National University of Singapore, Singapore

Farnoosh Pahlevanzadeh
Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran

Ballambettu Chandrasekhara Pai
*Council of Scientific & Industrial Research, National
Institute for Interdisciplinary Science and Technology,
Trivandrum, Kerala, India*

Sushanta K. Panigrahi
Indian Institute of Technology Madras, Chennai, India

Gururaj Parande
National University of Singapore, Singapore

P. Penjumras
*Universiti Putra Malaysia, Selangor, Malaysia and
Maejo University-Phrae Campus, Phrae, Thailand*

José Pérez-González
*Instituto Politécnico Nacional, Escuela Superior de Física
y Matemáticas, Ciudad de México, México*

Resego R. Phiri
*Botswana International University of Science and
Technology, Palapye, Botswana*

Rebaone E. Phuti
*Botswana International University of Science and
Technology, Palapye, Botswana*

Shiv K. Prajapati
*Ram-Eesh Institute of Vocational and Technical
Education, Greater Noida, Uttar Pradesh*

Sumit Pramanik
*Department of Mechanical Engineering, SRM Institute
of Science and Technology, Kancheepuram, Tamil Nadu,
India*

Somasundaram Prasadh
National University Centre for Oral Health, Singapore

Jordi Puiggalí
*Chemical Engineering Department, Polytechnic
University of Catalonia, Barcelona, Spain*

Gaofeng Quan
Southwest Jiaotong University, Chengdu, China

Gholamreza Masoudi Rad
Petroleum University of Technology, Ahvaz, Iran

Saba Rafique
*Department of Pharmaceutics, Faculty of Pharmaceutical
Sciences, Government College University, Faisalabad,
Faisalabad, Pakistan*

Ashok M. Raichur
Indian Institute of Science, Bangalore, Karnataka, India

Ankush Raina
*Shri Mata Vaishno Devi University, Katra, Jammu,
India*

V.K. Bupesh Raja
*Sathyabama Institute of Science and Technology,
Chennai, India*

Dipen K. Rajak
*Sandip Institute of Technology and Research Centre,
Nashik, Maharashtra, India*

Thazhivilai Ponnu Devaraj Rajan
*Council of Scientific & Industrial Research, National
Institute for Interdisciplinary Science and Technology,
Trivandrum, Kerala, India and Academy of Scientific
and Innovative Research, Ghaziabad, New Delhi, India*

Vaishnavi Ratheesh
National University Centre for Oral Health, Singapore

Mahmood Razzaghi
*Advanced Materials Research Center, Department of
Materials Engineering, Najafabad Branch, Islamic Azad
University, Najafabad, Iran*

Fizza A. Razzaq
*Department of Pharmaceutics, Faculty of Pharmaceutical
Sciences, Government College University Faisalabad,
Faisalabad, Pakistan*

Mattli M. Reddy
Qatar University, Doha, Qatar

Penchal Reddy Matli
National University of Singapore, Singapore

Lingbao Ren
Xi'an Jiaotong University, Xi'an, China

Hadis Rostamabadi
*Gorgan University of Agricultural Sciences and Natural
Resources, Gorgan, Iran*

A.M. Saad
*Technical University of Malaysia Melaka, Durian
Tunggal, Melaka, Malaysia*

Biranchi N. Sahoo
*Sardar Vallabhbhai National Institute of Technology,
Surat, Gujarat, India*

J.S. Saini
*Thapar Institute of Engineering and Technology, Patiala,
Punjab, India*

M.A. Salim
*Technical University of Malaysia Melaka, Durian
Tunggal, Melaka, Malaysia*

Mohd S. Salit
University Putra Malaysia, Serdang, Selangor, Malaysia

Saad Salman

Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Yarjan A. Samad

University of Cambridge, Cambridge, United Kingdom

Houman Savoji

Institute of Biomedical Engineering, Department of Pharmacology and Physiology, Faculty of Medicine, University of Montreal, CHU Sainte Justine Research Center, Montreal TransMedTech Institute, Canada

Sankaranarayanan Seetharaman

National University of Singapore, Singapore

Alexander Seifalian

Nanotechnology and Regenerative Medicine Commercialisation Centre (NanoRegMed Ltd), London BioScience Innovation Centre, London, United Kingdom

Rajashekhara Shabadi

Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

Fahad H. Shah

University of Peshawar, Peshawar, Pakistan

Yasser Shahzad

Department of Pharmacy, COMSATS University Islamabad, Lahore, Pakistan

Rana A. Shakoor

Qatar University, Doha, Qatar

Zahra Shariatinia

Amirkabir University of Technology, Tehran, Iran

Safian Sharif

Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Mahsa Shirazi

Sharif University of Technology, Tehran, Iran

Jaspreet Singh

Thapar Institute of Engineering and Technology, Patiala, Punjab, India

Kulwinder Singh

Thapar Institute of Engineering and Technology, Patiala, Punjab, India

N. Singh

Guru Nanak Dev Engineering College, Ludhiana, India

Ramachandra Arvind Singh

Wenzhou University, Wenzhou, China

Rupinder Singh

Guru Nanak Dev Engineering College, Ludhiana, India

Sunpreet Singh

Guru Nanak Dev Engineering College, Ludhiana, India

Tajinder P. Singh

Thapar Institute of Engineering and Technology, Patiala, India

Sanaz Soleymani Eil Bakhtiari

Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

Tirumalai Srivatsan

The University of Akron, Akron, OH, United States

Shamsuddin Sulaiman

Universiti Putra Malaysia, Serdang, Selangor, Malaysia

Santhosh Suresh

National University Centre for Oral Health, Singapore

Haroon K. Syed

Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Ghazal Tadayyon

Trinity College Dublin, Dublin, Ireland

Yousef Tamsilian

Shahid Chamran University of Ahvaz, Ahvaz, Iran

Monica Tapia-Gaspar

Tecnologico de Monterrey, Escuela de Ingeniería y Ciencias, Monterrey, México

Muniba Tariq

The University of Lahore, Islamabad Campus, Islamabad, Pakistan

Sravya Tekumalla

Nanyang Technological University, Singapore

Satish Teotia

Khalifa University of Science & Technology, Abu Dhabi, United Arab Emirates

Mohamed Thariq

University Putra Malaysia, Seri Kembangan, Malaysia

Maryam Ahmadzadeh Tofighy

Iran University of Science and Technology, Tehran, Iran

Madhavi Tripathi

Indian Institute of Science, Bangalore, Karnataka, India

Mir Irfan Ul Haq

Shri Mata Vaishno Devi University, Katra, Jammu, India

Raymond Wong

National University Centre for Oral Health, Singapore

Keng S. Woon

National University of Singapore, Singapore

Hong Yang
Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Noorfaizal Yidris
*University Putra Malaysia, Serdang, Selangor Darul
Ehsan, Malaysia*

Rizal Zahari
*University Putra Malaysia, Serdang, Selangor Darul
Ehsan, Malaysia*

S. Abolfazl Zahedi
De Montfort University, Leicester, United Kingdom

Mingyang Zhou
*Science and Technology on Reactor System Design
Technology Laboratory, Nuclear Power Institute of
China, Chengdu, China*

EDITORIAL BOARD

Editor in Chief

Dermot Brabazon

I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin, Ireland

Section Editors

Manoj Gupta, Section 1: *Metal Matrix Composite Materials*

Department of Mechanical Engineering, NUS, Singapore

Dermot Brabazon, Section 2: *Polymer Matrix Composite Materials*

I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin, Ireland

Fatima Zivic, Section 3: *Ceramics Matrix Composites*

Faculty of Engineering, University of Kragujevac, Kragujevac, Serbia

Eva Pellicer, Section 4: *Smart Composite Materials*

Departament de Física, Universitat Autònoma de Barcelona, Campus de la UAB, Barcelona, Spain

Dermot Brabazon, Section 5: *Processing of Composite Materials and Physical Characteristics*

I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin, Ireland

Robertt Valente, Section 6: *Design Methods for Composite Materials*

Center for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro, Portugal

Mohamed El Mansori, Section 7: *Nature Based and Inspired Composite Materials*

Arts et Metiers Institute of Technology, Mechanics Surfaces and Materials Processing, HESAM Université, Châlons-en-Champagne, France
Texas A&M Engineering Experiment Station, Institute for Manufacturing Systems, College Station, Texas, United States

Lorna Fitzsimons, Section 8: *Life Cycle Analysis and Sustainability of Composite Materials*

Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering and the Water Institute, Dublin City University, Dublin, Ireland

Antonello Astarita, Section 9: *Joining of Composite Materials*

Department of Chemical, Materials and Industrial Production Engineering, University of Naples Federico II, Naples, Italy

PREFACE

This is the first *Encyclopedia of Materials: Composites* published by Elsevier which presents a vast and widely encompassing content in the area of composite materials science and engineering. Composite materials have become even more important and ubiquitous over the recent decades due to the many advantages that they can provide over single monolithic materials. This includes improvements in the properties such as the physical, electrical, chemical, optical and magnetic properties which can be achieved by combining two or more materials.

The two main types of composites, Metal and Polymer matrix based, are presented in detail within Sections 1 and 2 respectively while Ceramic matrix composites are presented in Section 3. Smart composites which is an area that is growing fast with increasing industrial relevance is covered in Section 4. Assessing the properties of composite materials thereby enabling their application is a crucial aspect of composite materials development and usage. As such, Section 5 presents the testing methods used and property results from the testing of composite materials. The design of composite materials is covered in Section 6. The recyclability and sustainability of materials used in products is an ever more important topic. There are some challenges to achieve well the recyclability of composite constructs. The Encyclopedia presented two Sections covering this one (Section 7) covering nature based composites and another covering the life cycle analysis of composite materials (Section 8). In the last section of the Encyclopedia, Section 9 covers how to join composite materials together and with more conventional monolithic materials.

As an Encyclopedia, these sections were prepared to be the primary central source of background knowledge for undergraduate, postgraduate and researchers studying or working with composites. The audience of this work covers both academic and industrial researchers. In today's composite materials market, engineers, architects, and even policy makers, need reference literature where to find definitions, concepts and state-of-the-art knowledge. As such this Encyclopedia will be an invaluable reference for engineers, architects, scientists, and policy makers.

Each section contains articles written by world experts in their area. As well as providing the latest background information, the state of the art in the niche areas is presented in the individual articles. A particular concern in preparing these articles by the authors and Section editors was to make the content as accessible as possible to the reader. This is important given the multi-disciplinary nature of people working on the development and implementation of composite materials.

I take this opportunity to thank the 337 authors from across the world who have contributed the 171 articles to this Encyclopedia. It has been enjoyable to work with you are encouraging to see your expertise, interest and desire to help others from your contribution. With the many co-authored articles, there has been extensive collaboration which has resulted in a more informed and well-presented Encyclopedia content for the reader.

I am indebted also to the members of the Editorial team who have worked many long hours over the last couple of years to provide feedback and iterate on articles with the authors. The Editorial team have collectively many years of expertise working in their research areas. This team was formed via a variety networking events including conferences such as ESAFORM and Global Conference on Nanomaterial Forming (Manoj Gupta, Robertt Valente, Antonella Astarita), EU research projects and COST Actions (Fatima Zivic and Eva Maria Pellicer), and via other Dublin City University and sustainable engineering networking events (Mohamed El Mansori and Lorna Fitzsimons). I thank the Elsevier Major Reference Works team who supported in a professional manner the compiling of this work. In particular, I thank Laura Jackson, Sajana P K, and Ruth Rhodes for their direction and support throughout the preparation of this Encyclopedia.

Dermot Brabazon
May 2021

Introduction to Metal Matrix Composite Materials: An Introduction

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introducing Composites

Composite refers to a material that is an outcome of unification of two different class of materials ([Fig. 1](#)) ([Ceschini et al., 2016](#); [Gupta and Sharon, 2011](#)). To note that composites were used in making bricks in prehistoric times and more importantly by nature in providing functionality to both plants and animals including humans. The keen observations made by humans led to development of modern composites including MMCs.

Composites can traditionally be classified using two approaches:

- (1) Matrix based.
- (2) Reinforcement based.

Schematics of these approaches to classify composites are shown in [Figs. 2 and 3](#), respectively. For matrix-based classifications, there may be other matrices such as Carbon matrix but they are more specialized types and do not come under mainstream composites.

Based on reinforcements, the composites can be classified as (see [Fig. 4](#)):

- (1) Continuously reinforced composites.
- (2) Discontinuously reinforced composites.

Continuously reinforced composites display anisotropic properties while discontinuously reinforced composites exhibit isotropic properties.

Based on length scale of reinforcements, the composites can further be classified as shown in [Fig. 5](#). Each of these types of composites have their unique advantages and limitations and their selection for industrial applications depends largely on the properties requirements of the end applications.

Selection of metallic matrix for a composite is based on the combination of chemical, physical, thermal and mechanical properties and cost factor depending on the requirements of end applications ([Fig. 6](#)) ([Lloyd, 1994](#); [Ibrahim et al., 1991](#)).

Similarly, the selection of reinforcement is based on similar factors including the directionality of properties (isotropic or anisotropic) and compatibility with matrix (see [Fig. 7](#)).

Metal Matrix Composites – Matrix and Reinforcements

Metal matrix composites (MMCs) represent conscious unification of metallic matrix and at least one reinforcement. The reinforcement can be ([Ceschini et al., 2016](#); [Gupta and Sharon, 2011](#); [Lloyd, 1994](#); [Ibrahim et al., 1991](#); [Jayalakshmi and Gupta, 2015](#)):

- (1) Metallic.
- (2) Ceramic (oxides, carbides, nitrides, borides).
- (3) Intermetallic.
- (4) Carbon based (CNT, graphene, buckyball, graphene oxide).
- (5) Hollow (cenospheres, metal or ceramic based).
- (6) Hybrid (combination of above and combination of length scales).
- (7) Amorphous.
- (8) Multicomponent alloys.

Most commonly used metallic matrices include but not limited to the following:

- (1) Aluminum and its alloys.
- (2) Magnesium and its alloys.
- (3) Iron and its alloys.
- (4) Nickel and its alloys.
- (5) Copper and its alloys.
- (6) Tin and its alloys.
- (7) Titanium and its alloys.

Major factors that govern the properties of MMCs are based on: (a) Processing and (b) Constituents and (c) Microstructure (see [Fig. 8](#)) ([Lloyd, 1994](#); [Ibrahim et al., 1991](#)).

The capability of primary processing type on the microstructure and properties realization is expressed in [Fig. 9](#).



Fig. 1 Definition of composite.

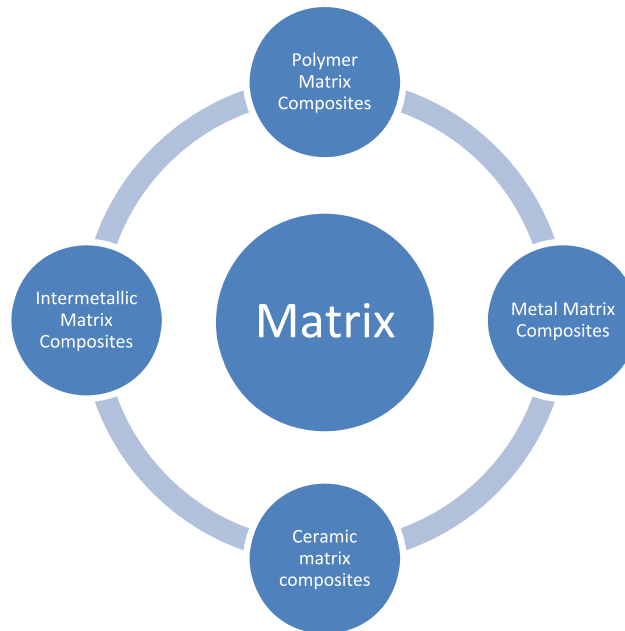


Fig. 2 Matrix based classification of composites.

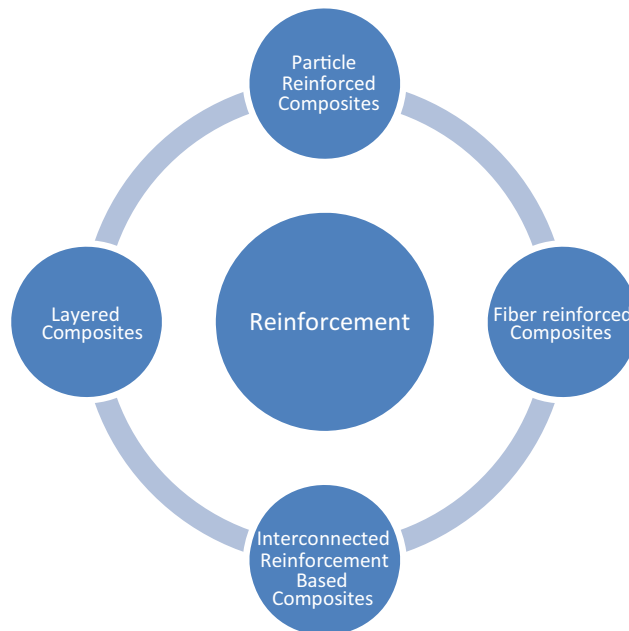


Fig. 3 Reinforcement based classification of composites.

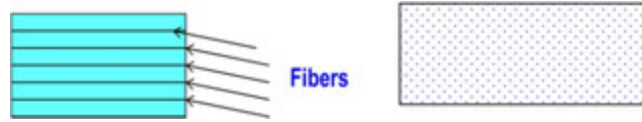


Fig. 4 Continuously (left) and discontinuously (right) reinforced composites.

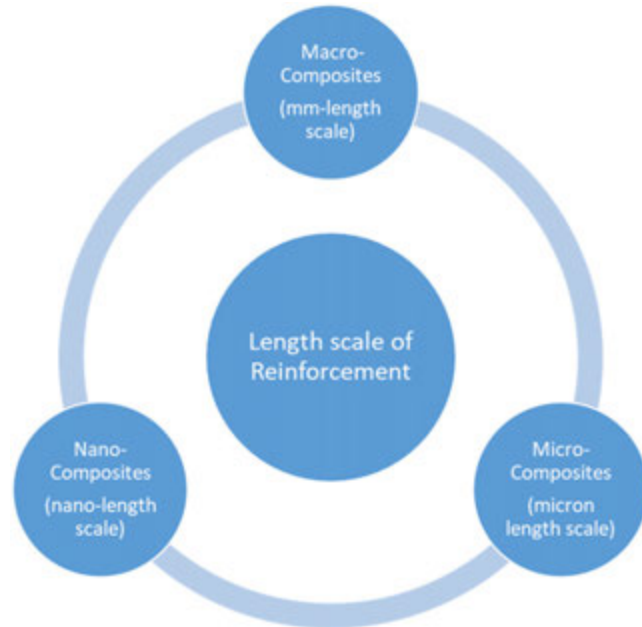


Fig. 5 Classification of composites based on length scale of reinforcement.

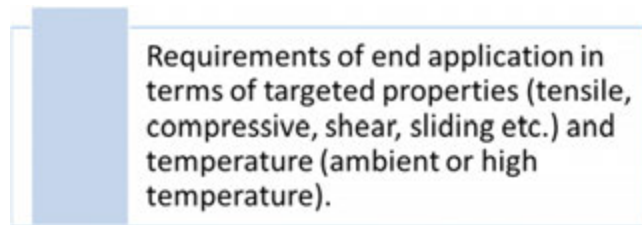


Fig. 6 Factors related to selection of matrix.

The major (not limited to) matrix and reinforcement related factors that govern the end properties of MMCs are shown in **Figs. 10** and **11**, respectively (Ceschini *et al.*, 2016; Gupta and Sharon, 2011; Lloyd, 1994; Ibrahim *et al.*, 1991).

Metal Matrix Composites – Processing

As indicated in **Fig. 9**, MMCs can primary processed using following economically viable routes (Lloyd, 1994; Ibrahim *et al.*, 1991):

- (1) Liquid phase methods.
- (2) Solid phase methods.
- (3) Two phase methods.

There are other methods that are being researched but those methods are still in the developmental stages for scalable and/or economical production. The liquid, solid and two-phase methods are listed in **Figs. 12–14**.

Among the liquid phase methods, the one including ultrasonic probes/transmitters are relatively new developments that have shown promising results.



Fig. 7 Factors controlling selection of reinforcement.

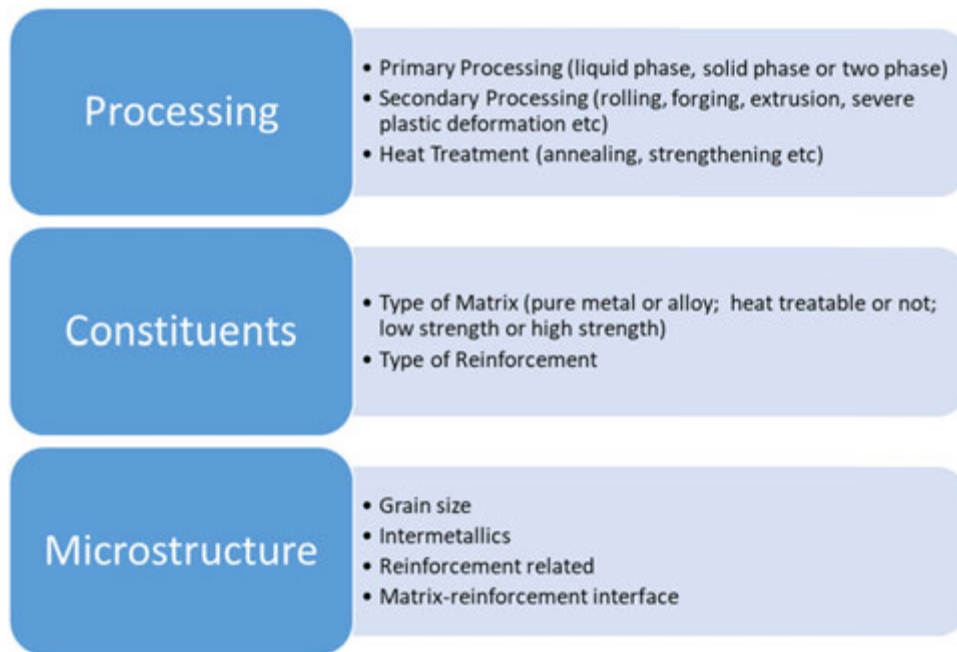


Fig. 8 Major factors governing the properties of MMCs.

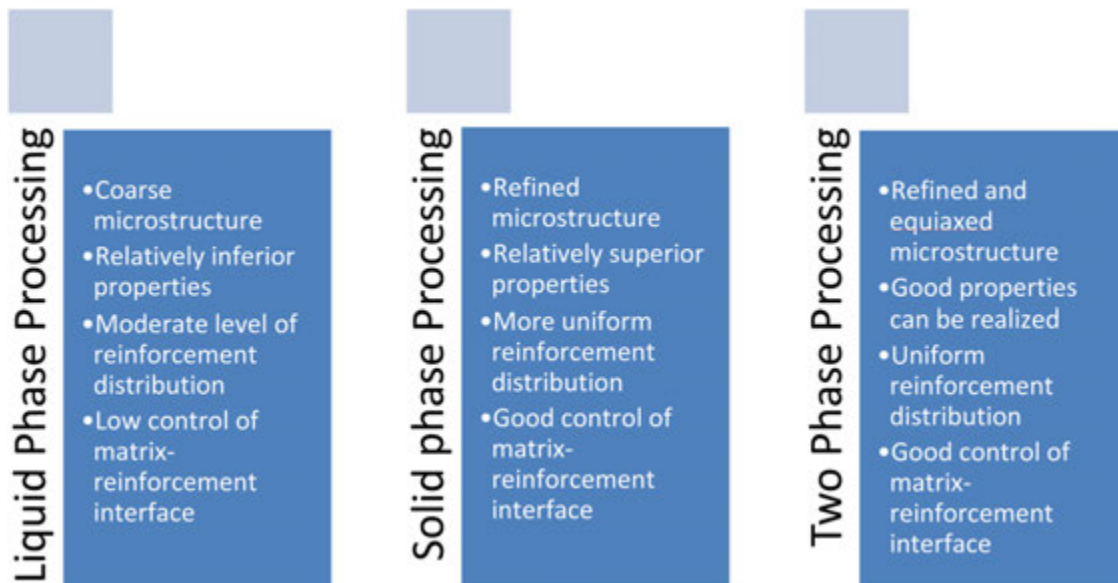


Fig. 9 Processing type effects on microstructure and properties of MMCs.

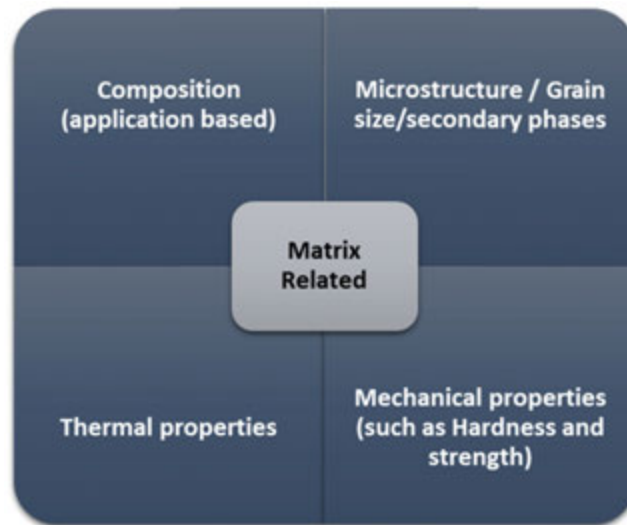


Fig. 10 Matrix related factors governing the properties of MMCs.

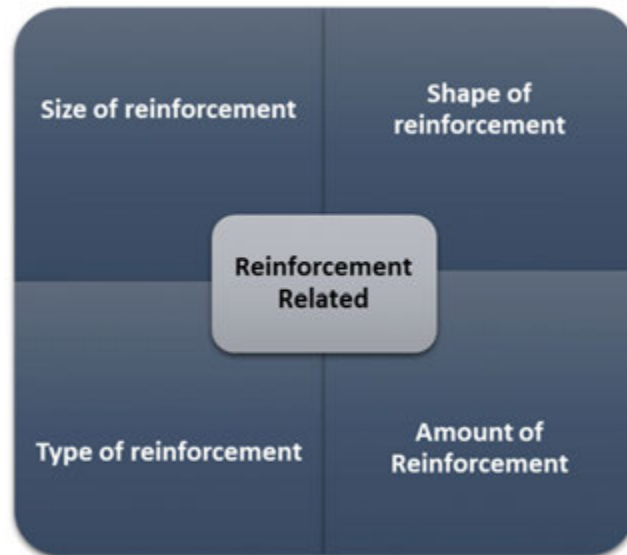


Fig. 11 Reinforcement related factors governing the properties of MMCs.

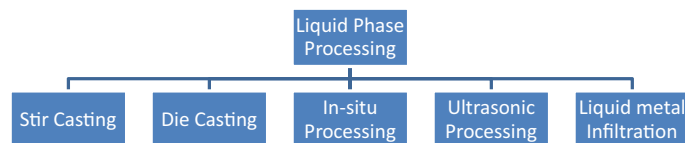


Fig. 12 Most commonly used/researched methods to synthesize MMCs using liquid phase processing.

Among powder metallurgy methods, use of microwave sintering (Gupta and Leong, 2007), spark plasma sintering (Azarniya *et al.*, 2017), flake powder metallurgy (Xu *et al.*, 2017), molecular level mixing (Bakshi *et al.*, 2010) and friction stir processing (Eskandari *et al.*, 2016) are relatively new processes with significant potential.

Two phase methods probably were most exciting from metallurgical point of view, however, their utility in industrial processing is limited. Disintegrated melt deposition technique is the latest process in this category with potential of scalability at a very low equipment and infrastructural costs.

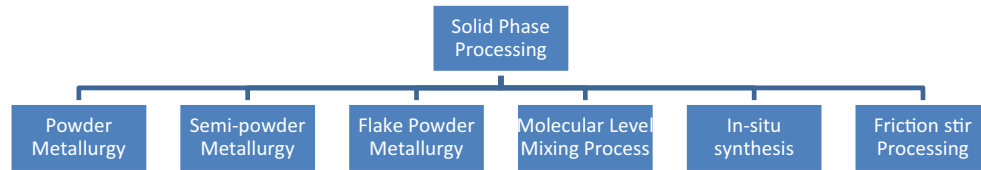


Fig. 13 Most commonly used/researched methods to synthesize MMCs using solid phase processing.

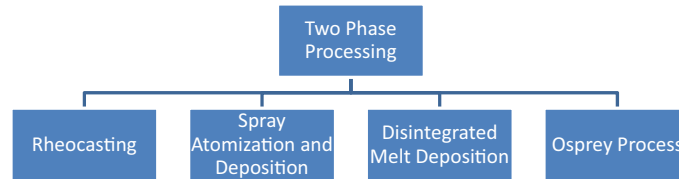


Fig. 14 Most commonly used/researched methods to synthesize MMCs using two phase processing.

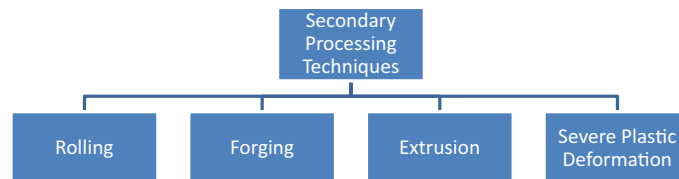


Fig. 15 Most commonly used/researched secondary processing methods.

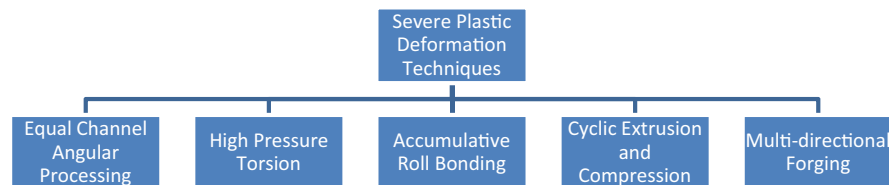


Fig. 16 Most commonly used/researched severe plastic deformation methods.

The selection of the process in each category depends largely on the:

- (1) Size of the part.
- (2) Geometry of the part.
- (3) Number of parts to be produced.
- (4) Microstructural characteristics expected in parts.
- (5) Level of properties expected from the end part.
- (6) Price tag of the final part.

Depending on the end application, at times the MMC billets are also secondary processed to further enhance their microstructural characteristics and properties. Common secondary processing techniques are indicated in [Fig. 15](#).

In more recent times, efforts are continuously made to significantly enhance the properties of MMCs using severe plastic deformation methods. Some of the promising methods severe plastic deformation processes used on bulk materials are listed in [Fig. 16](#).

Metal Matrix Composites – Properties

Like other structural materials, MMCs are used where certain enhanced functionalities from metallic materials is expected in end applications due to the more demanding nature of emerging end applications. Most commonly investigated properties where enhancement is expected include ([Ceschini et al., 2016](#); [Gupta and Sharon, 2011](#); [Lloyd, 1994](#); [Ibrahim et al., 1991](#)):

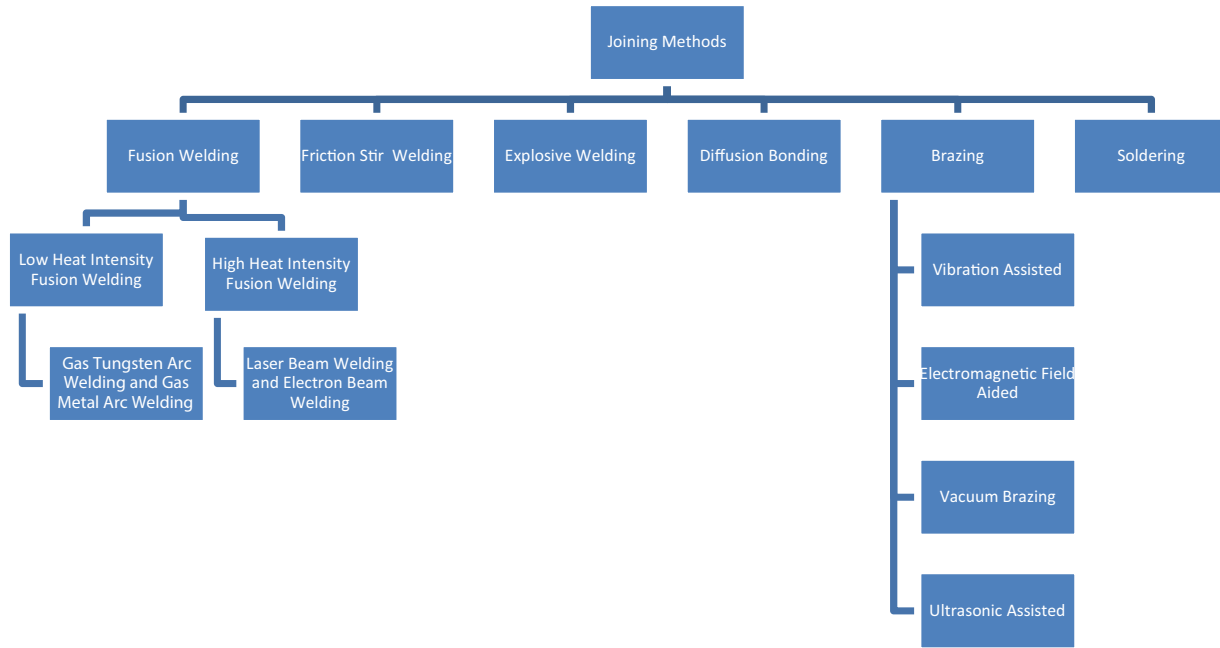


Fig. 17 Commonly used/researched joining methods for MMCs.

- (1) Coefficient of thermal expansion: For dimensional stability of parts.
- (2) Elastic modulus: For stiffness based designs.
- (3) Damping: For mitigating vibrations in structures that are prone to it.
- (4) Hardness: For erosion, wear and crack initiation resistance.
- (5) Strength: Tensile, compressive, flexural, torsional and high temperature.
- (6) Fatigue: Cyclic loading is common in many applications.
- (7) Creep: To enhance the working temperature limits.
- (8) Wear resistance: For sliding parts.
- (9) Erosion resistance: Such as in hydro-thermal power plants.

A detailed analysis of these properties can be found elsewhere in this encyclopedia and will not be discussed here.

Metal Matrix Composites – Joining

For industrial applications, joining of MMCs with MMCs or other metallic materials is required. Welding is one of the common practice for the same. Different joining methods that have evolved and used are indicated in [Fig. 17](#) (Ellis, 1996; Prater, 2011).

More recent development in joining of composites can be referred to in another article in this encyclopedia.

Metal Matrix Composites – Machining

Machining is an important operation before a part is assembled into a device. Machining is done on both the cast and wrought parts to different extents. Conventional machining processes such as turning, milling, drilling and wire cutting (EDM) are used for machining MMCs (Lane, 1992; Gururaja *et al.*, 2013). As traditional MMCs are reinforced with ceramic reinforcements which are typically harder than materials used for making conventional tools (e.g. tool steels), the wear or deterioration of tools increases faster affecting the surface characteristics of material that is machined. The problem is more severe when the micron and higher length scale ceramic reinforcements are used as they can be loaded to a higher extent. Similarly, reduction in particle diameter also assist in reducing tool wear and in that context, it is anticipated that nano-composites will perform better than microcomposites (Lane, 1992). Diamond coated tools in that respect display better machining performance.

While investigating a machining process, researchers typically focus and optimize on the following parameters (Gururaja *et al.*, 2013):

- (1) Workpiece material: Nature of metallic matrix and reinforcement associated variables.
- (2) Type of tool used: Polycrystalline diamond tools are most favored.

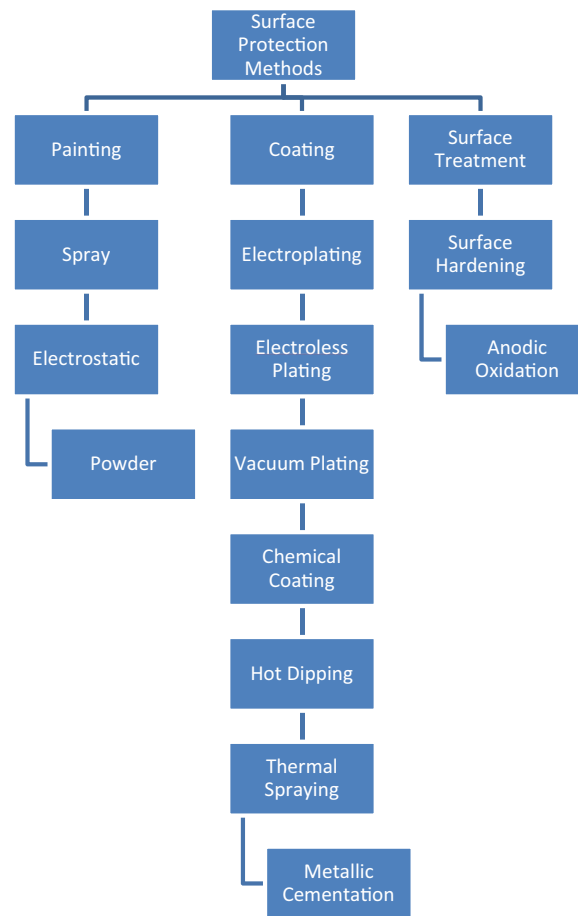


Fig. 18 Commonly used/researched surface protection methods for MMCs.

- (3) Use of lubricant.
- (4) Cutting speed.
- (5) Cutting depth.

It was emphasized by researchers that due to above mentioned factors and complexity of machining processes, detailed optimization of the parameters is important to ensure minimal tool wear and to realize desirable surface finish. Latest and detailed information on high performance machining of MMCs can be referred to in another article on machining in this encyclopedia in the Metal Matrix Composites section.

Metal Matrix Composites – Surface Protection

Surface protection of metallic surfaces is important and MMCs are no exception. The common purposes of providing surface protection include:

- (1) Corrosion protection: Both dry and wet.
- (2) Mechanical protection such as against scratches.
- (3) Erosion resistance.
- (4) Wear resistance.

Surface protection methods primarily include:

- (1) Painting: Layers of organic substances such as use of paints containing acrylic/vinyl resins.
- (2) Coating: Use of metallic layers or ceramic powders.
- (3) Surface treatment: Altering the surface characteristics using processes such as carburizing, laser hardening etc.

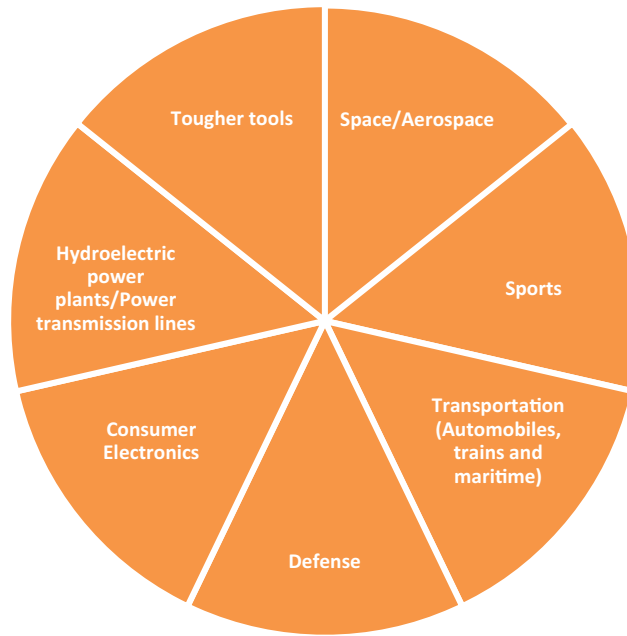


Fig. 19 Potential sectors for application of MMCs.

Various types under these categories are shown in [Fig. 18](#) and discussed in details elsewhere in this Encyclopedia.

Metal Matrix Composites – Applications

Metal matrix composites are actively been looked into many structural and non-structural applications and most prominent of them are indicated in [Fig. 19](#) ([Ceschini et al., 2016](#); [Gupta and Sharon, 2011](#); [Lloyd, 1994](#); [Ibrahim et al., 1991](#)). Main physical, thermal, mechanical and surface properties that are actively looked for these applications are:

- (1) Density: For light weighting.
- (2) Coefficient of thermal expansion: For dimensional stability.
- (3) Thermal conductivity: Heat management in transportation and electronic sectors.
- (4) Elastic modulus: For improving stiffness and deflection resistance.
- (5) Hardness: For erosion resistance such as in hydroelectric thermal plants.
- (6) Wear resistance: For sliding resistance such as in oil and gas and transportation sectors.

Most of the abovementioned properties can be easily tailored and realized using MMC technology. Besides investigators are looking into the possibility of using MMC technology in many other more specific applications which include and not restricted to the following:

- (1) Infrastructural applications.
- (2) Biomedical applications ([Gupta and Meenashisundaram, 2015](#)).
- (3) Recreational applications.
- (4) Home appliances such as CermeTi knives.
- (5) Nuclear applications for thermos-neutron shielding.

Challenges With MMC Technology

Active research in MMCs has almost spanned five decades and tremendous lessons are learnt on the fundamental principles governing their microstructure and properties. Researchers have convincingly established the efficacy of many formulations at lab scale and certain leading multinational companies have shown the capabilities to convert them into industrial products. However, the issue of scalability to synthesize MMCs using liquid metallurgy based high volume production routes with microstructural consistency is still a big issue for many countries for their widespread use. More involvement of industry is required to take these highly tailorable and property specific materials to the next level.

References

- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2016. Aluminum and Magnesium Metal Matrix Nanocomposites. Springer. (ISBN: 978-981-10-2680-5 (Print) 978-981-10-2681-2 (Online)).
- Azarniya, A., Azarniya, A., Sovizi, S., *et al.*, 2017. Physicomechanical properties of spark plasma sintered carbon nanotube-reinforced metal matrix nanocomposites. *Progress in Materials Science* 90, 276–324.
- Bakshi, S.R., Lahiri, D., Agarwal, A., 2010. Carbon nanotube reinforced metal matrix composites – A review. *International Materials Reviews* 55 (1), 41–64.
- Ellis, M.B.D., 1996. Joining of Al-based metal matrix composites – A review. *Materials and Manufacturing Processes* 11 (1), 45–66. doi:10.1080/10426919608947460.
- Eskandari, H., Taheri, R., Khodabakhshi, F., 2016. Friction-stir processing of an AA8026-TiB₂-Al₂O₃ hybrid nanocomposite: Microstructural developments and mechanical properties. *Materials Science and Engineering A* 660 (13), 84–96.
- Gupta, M., Meenashisundaram, G.K., 2015. *Insight into Designing Biocompatible Magnesium Alloys and Composites*. Springer.
- Gupta, M., Wong Wai Leong, E., 2007. *Microwaves and Metals*. Singapore: John Wiley and Sons (Asia) Pte Ltd, (ISBN: 978-0-470-82272-2; ISBN: 978-0-470-49417-2).
- Gupta, M., Sharon, N.M.L., 2011. *Magnesium, Magnesium Alloys and Magnesium Composites*. John Wiley.
- Gururaja, S., Ramulu, M., Pedersen, W., 2013. Machining of MMCs: A review. *Machining Science and Technology: An International Journal* 17 (1), 41–73.
- Ibrahim, I., *et al.*, 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science* 26 (5), 1137–1156.
- Jayalakshmi, S., Gupta, M., 2015. *Metallic Amorphous Alloy Reinforcements in Light Metal Matrices*. Springer.
- Lane, C., 1992. Machinability of aluminium composites as a function of matrix alloy and heat treatment. In *Proceedings of the Machining of Composite Materials Symposium*. Chicago, IL: ASM Material Week.
- Lloyd, D., 1994. Particle reinforced aluminium and magnesium matrix composites. *International Materials Reviews* 39 (1), 1–23.
- Prater, T., 2011. Solid-state joining of metal matrix composites: A survey of challenges and potential solutions. *Materials and Manufacturing Processes* 26 (4), 636–648. doi:10.1080/10426914.2010.492055.
- Xu, R., Tan, Z.Q., Xiong, D.B., *et al.*, 2017. Balanced strength and ductility in CNT/Al composites achieved by flake powder metallurgy via shift-speed ball milling. *Composites Part A: Applied Science and Manufacturing* 96, 57–66.

Fundamentals of Metal Matrix Composites

Sankaranarayanan Seetharaman and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composites (MMCs) comprise of a continuous matrix of metallic alloys together with ceramic reinforcements, or metallic phases (Clyne and Withers, 1995). They offer a wide range of opportunities in various applications such as automobile, power train, aerospace, consumer electronics, packaging, and sports due to improved mechanical properties, wear resistance, creep resistance, damping characteristics, and reduced thermal expansion characteristics (Sijpkens and Vergouwen, 2004; Kainer, 2006; Barrett, 2017) (Fig. 1).

Fig. 2 Shows some of the commonly used matrix materials which include aluminum, copper, magnesium, titanium, nickel, steel whose properties are listed in Table 1. While MMCs based on aluminum, magnesium, and titanium alloys are the excellent candidates for lightweight structures in automotive, aerospace, and defense applications (Adebisi *et al.*, 2011; Jayalakshmi and Gupta, 2015), MMCs based on steel, nickel, and copper alloys are highly recommended for tooling, heavy industries, and electronic packaging, respectively.

In general, the reinforcement phases are hard and strong, and they are known to exhibit good thermal stability and Young's modulus. Hence, the inclusion of reinforcements can improve the performance of matrix material (Ashby, 2005; Callister and Rethwisch, 2007). Some of the commonly used reinforcements are shown in Figure and their properties are listed in Table 2. Based on the size and shape, reinforcements can be broadly classified into continuous and discontinuous reinforcement forms (Chawla and Chawla, 2004). The most common continuous reinforcement are the carbon or ceramic fibers. As these fibers are brittle and flaw sensitive, they are often provided protective coatings to avoid any unwanted chemical reactions and to improve the bonding/wetting characteristics. The fiber reinforcements are also known to exhibit size effects (i.e., the strength of these fibers decreases as the length increases), and they can be further classified into long or short fibers. Similarly, discontinuous reinforcement includes ceramic and metallic particulates in the size range from few nanometers to few hundred micrometers which are known to develop MMCs with isotropic properties (Chawla and Chawla, 2004; Kainer, 2006).

Classification of Metal Matrix Composites

Based on the type of reinforcement, MMCs are classified into (1) fiber reinforced MMCs, (2) particle reinforced MMCs, and (3) multi-layered laminates (Fig. 3). The fiber composites can be further classified as continuous and discontinuous fiber reinforced composites.

Fiber Reinforced MMCs

The fiber reinforced MMCs can be broadly classified into either (i) long, or (ii) short fiber reinforced metal matrix composites. While the long-fiber reinforced composites consists of a dispersed phase in the form of continuous fibers (length $> 100 \times$ diameter), the fiber lengths are often short ($< 100 \times$ diameter) in the case of short fiber reinforced MMCs.

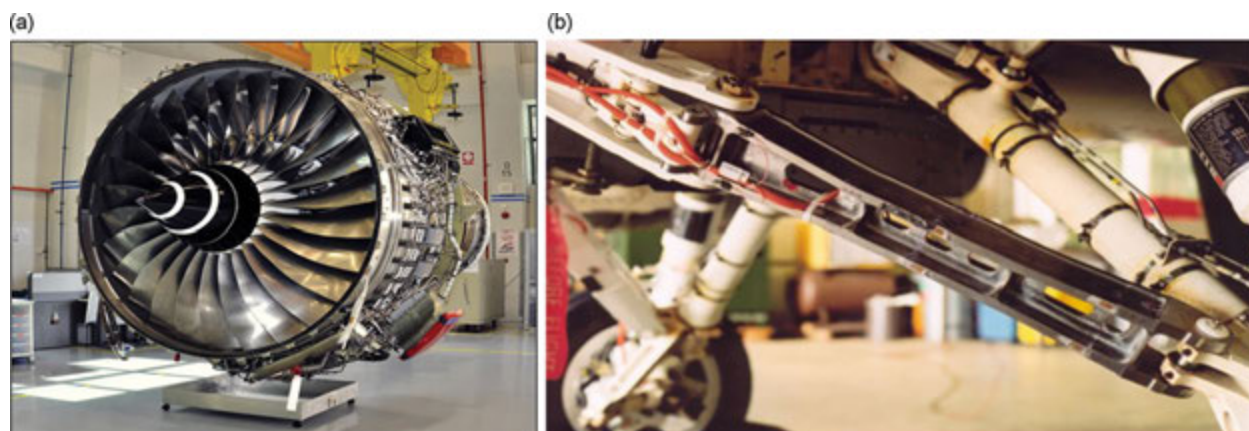


Fig. 1 (a) Turbofan made using MMC and (b) Structural component in F16 Falcon landing gear made using SiC monofibers reinforced Ti MMC. Courtesy: Barrett, T., 2017. The Future of Metal Is in Matrix Composites. Available at: <https://www.machinedesign.com/materials/article/21835569/the-future-of-metal-is-in-matrix-composites>. Sijpkens, T., Vergouwen, P., 2004. Composite materials for structural landing gear components. In: ERF 2004, 38. Available at: https://dspace-erf.nlr.nl/xmlui/bitstream/handle/20.500.11881/282/38_sijpkens.pdf?sequence=1&isAllowed=y.

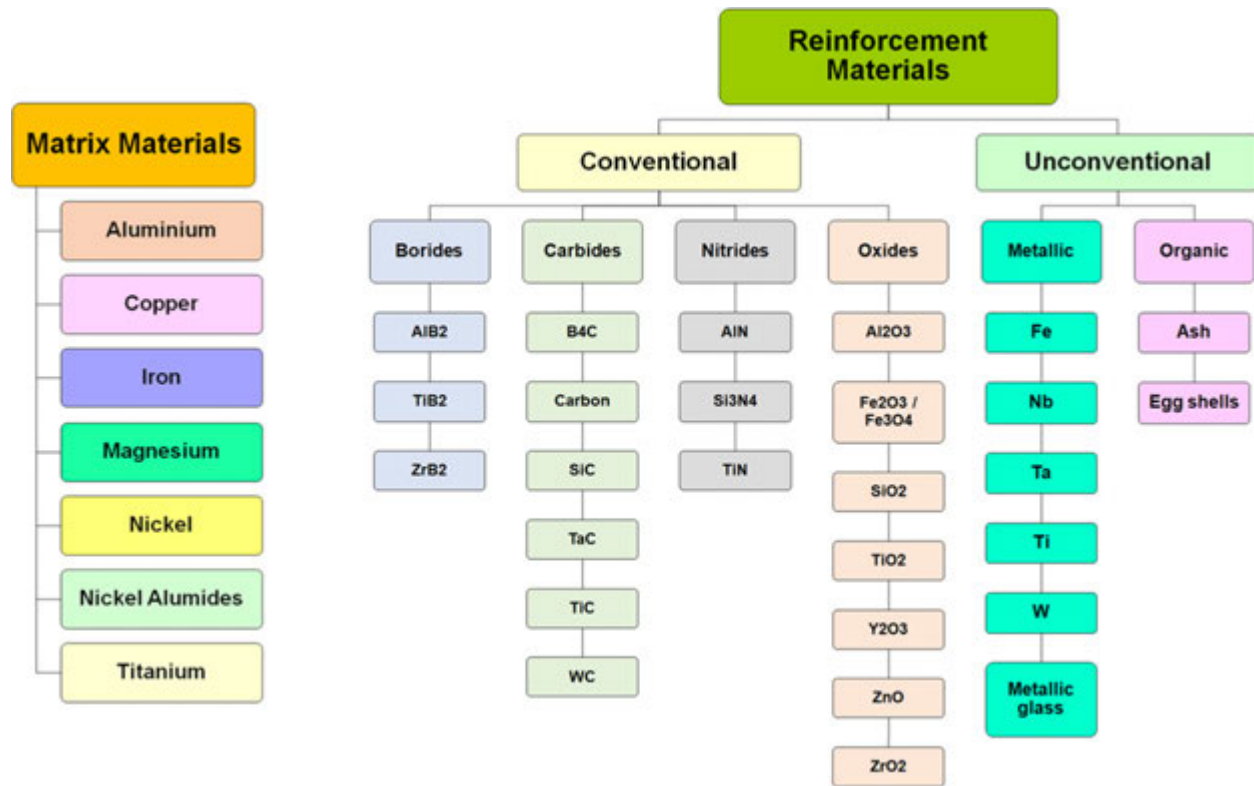


Fig. 2 Usage of matrix and reinforcement materials in MMCs.

Table 1 Properties of common matrix materials

Base matrix alloy	Density (g/cc)	Modulus (GPa)	Yield strength (MPa)	Ductility
Magnesium	1.74–1.95	42–47	70–400	3.5–18
Aluminum	2.5–2.9	68–82	30–500	1–44
Titanium	4.4–4.8	90–120	250–1250	1–40
Steels	7.1–8.0	187–215	240–690	18–31
Nickel	7.75–8.65	150–245	300–1900	0.5–60
Copper	8.93–8.94	112–148	300–500	3–50

Table 2 Properties of common reinforcement materials

Metal	Crystal structure	Density (g/cm ³)	Melting point (°C)	Thermal conductivity	Thermal expansion coefficient	Mohr hardness	Modulus (GPa)
Al ₂ O ₃	Hex.	3.9	2050	25	8.3	6.5	410
AlN	Hex.	3.25	2300	10	6	–	350
B ₄ C	Rhom.	2.52	2450	29	5–6	9.5	450
BN	Hex.	2.2	3000	25	3.8	1–2	90
SiC	Hex.	3.21	2300	59	4.7–5	9.7	480
Si ₃ N ₄	α-trigonal/β-Hex./γ-cub	3.29	1900	29	3.3	–	310
TiB ₂	Hex.	4.5	2900	27	7.4	–	370
TiC	Cub.	4.93	3140	29	7.4	–	320
TiN	Cub.	5.24	2950	29	9.4	–	600
WC	Hex	15.7	2800	110	5.2	9.5	690

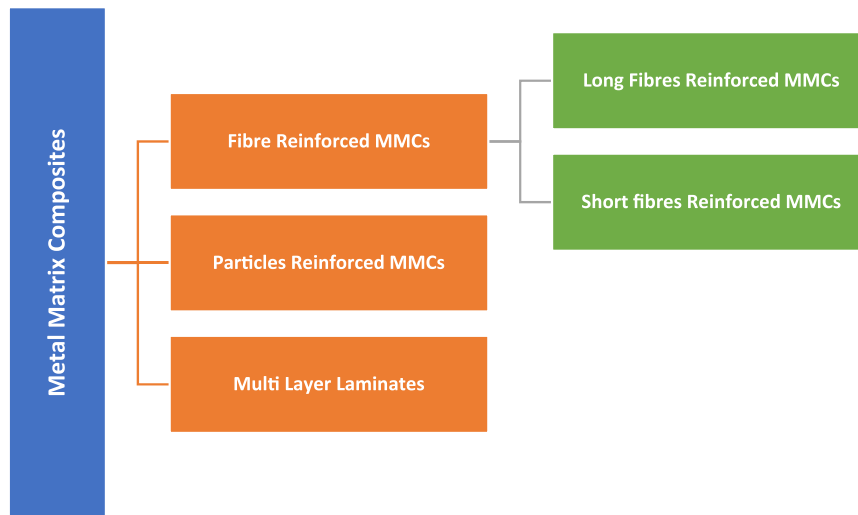


Fig. 3 Classification of metal matrix composites.

Particulate Composites

Particulate composites consist of a matrix reinforced by particles that are dispersed randomly or with a well-defined orientation.

Nanocomposites

In particulate composites, when one of the dimensions of the particulate reinforcement is less than 100 nm, the resulting composite is referred to as nanocomposite. Recently, metal matrix composites containing nanoscale reinforcements are receiving stupendous attention as the low volume dispersion of hard and strong reinforcing phases in nano-length scale contributes significantly towards the strengthening of the matrix material. Unlike micron and sub-micron length scale reinforcement addition, the efficient dispersion of nanoscale reinforcement improves the strength of matrix material without adversely affecting the ductility (Goh *et al.*, 2006b; Casati and Vedani, 2014; Gupta and Wong, 2015).

Carbon nanotubes reinforced MMCs

The outstanding strength properties of carbon nanotubes (11–150 GPa) make them highly suitable for use as particulate reinforcements in various metal matrix composites (Popov, 2004; Goh *et al.*, 2006a; Esawi and Farag, 2007; Bakshi *et al.*, 2010; Neubauer *et al.*, 2010; Bhat *et al.*, 2011; Casati and Vedani, 2014). Although several publications report the exceptional strengthening promise of multiwalled CNT, defect free processing of CNT reinforced MMCs is challenging. Some of the recent research works also explored the effects of nanoscale graphene platelets (Saboori *et al.*, 2018) and other advanced engineering materials such as metallic glass (Jayalakshmi *et al.*, 2018) and shape memory alloys (Ferguson *et al.*, 2014; Rohatgi, 2014) as discontinuous reinforcement.

Laminate Composites

Composite laminates consist of multiple layers of sheet laminates made of the matrix and reinforcement materials stacked and cemented in a specific pattern in order to achieve the desired strength. Based on the stacking sequence, the composite laminates are classified into angle and cross-ply laminates which can be either symmetric, antisymmetric, or balanced. Fig. 4 shows the construction of a lightweight laminated composite (0.16 kg) developed to replace the aluminum heat sink (0.29 kg) of printed circuit boards.

Processing of Metal Matrix Composites

A variety of methods can be employed in the fabrication of metal matrix composites and they can be broadly grouped under either liquid or solid-state processing methods. Similarly, based on the nature of reinforcement addition, the processing methods can be either ex-situ or in-situ processing.

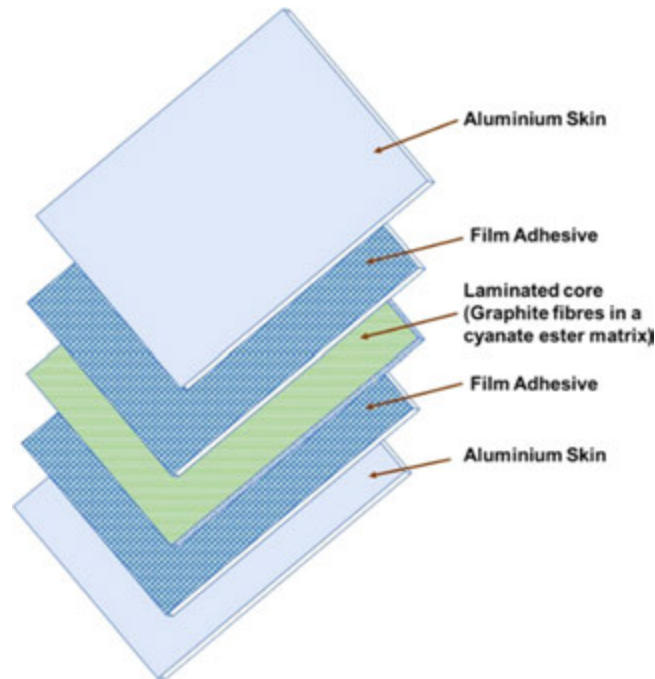


Fig. 4 Lightweight laminated composite heat sink developed for printed circuit boards. Redrawn from Holz, J.M., Niemeyer, L., Puckett, D., 2000. Composite-Material Heat Sink for Printed-Circuit Boards, Technical Support Package. GSC-14142. Goddard Space Flight Center. Available at: <https://www.techbriefs.com/component/content/article/tb/techbriefs/materials/6720>.

Liquid State Processing

Liquid state processing generally involves the preparation of a composite slurry through the dispersion of reinforcement materials into a molten matrix which is then followed by the solidification into required shape. Here, the reinforcement dispersion can be performed using multiple ways such as: (1) melt infiltration, (2) stir casting or compo-casting, and (3) melt deposition.

Melt infiltration

Melt infiltration involves either spontaneous or forced infiltration of a liquid metal alloy into a porous preform containing fibers/whiskers reinforcements upto 70 vol% (Kainer, 2006). The spontaneous infiltration is also known as pressure less infiltration in which no external pressure or force is used to process MMCs based on Al-Si, Al-Mg, and Al-Zn alloys with better flowability. However, the poor wettability between the matrix and the reinforcing phase slows down the fabrication process resulting in undesirable reaction products at the interface. Several studies have reported an improvement in the wettability through activators or processing in nitrogen atmosphere. In forced infiltration process, the infiltration of molten metal into the porous reinforcement is achieved through the application of external pressure or by using mechanical force as shown below to overcome the issues associated with poor wetting and adhesion characteristics.

Pressure die infiltration:

In pressure die infiltration, the molten composite slurry is force injected into the mold using an injection barrel (Cook and Werner, 1991; Altinkok *et al.*, 2003). The key advantages of this methods are its low cost and the high precision capability (Figs. 5 and 6).

Gas pressure infiltration:

In this process, the reinforcement preforms are infiltrated using pressurized inert gas in which the gas pressure can be applied in two ways: (1) application of gas pressure to the melt surface after dipping the preform into the melt for infiltration, (2) the applied gas first presses the molten bath into the preform and then infiltrates the bath (Daoud, 2004). Generally, the gas pressure is applied in combination with vacuum at the other end of preform to avoid air entrapment to help easy penetration at lower pressures. Since reaction times are relatively short, fibers are subjected to less damage (compared to other processes) and the reactive materials can be processed without difficulty. Also, this method can be used for large-scale production of the composite materials.

Ultrasonic infiltration:

In this process, the pressure waves generated by ultrasonic vibrations assists in the acoustic cavitation and the collapse of bubbles originating close to the molten metal helps in the penetration of molten metal into the reinforcement preform (Matsunaga *et al.*, 2007). Fig. 7 shows the ultrasonic infiltration experimental setup used to fabricated carbon fiber reinforced Al composite wires.

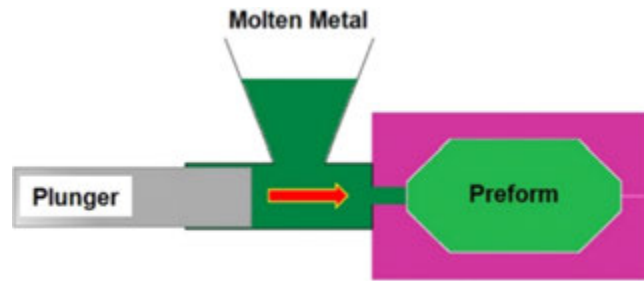


Fig. 5 Pressure die infiltration process. Redrawn from Garg, P., *et al.*, 2019. Advance research progresses in aluminium matrixcomposites: Manufacturing & applications. Journal of Materials Research and Technology. 8 (5), 4924-4939. doi:[10.1016/j.jmrt.2019.06.028](https://doi.org/10.1016/j.jmrt.2019.06.028).

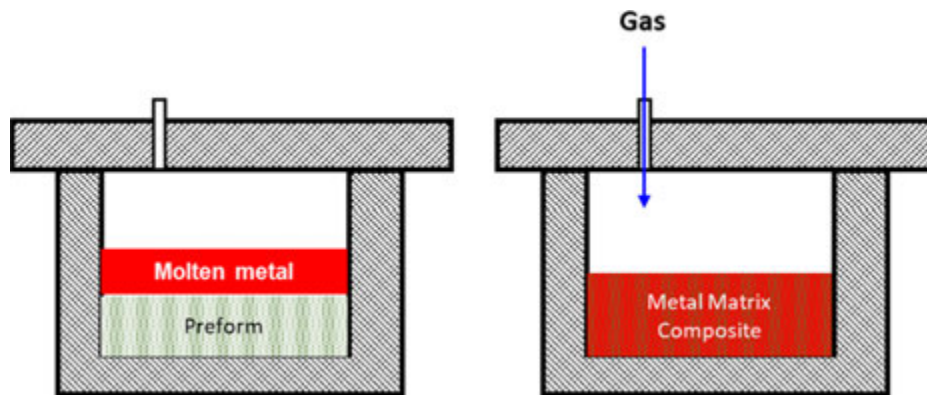


Fig. 6 Gas pressure infiltration. Redrawn from Garg, P., *et al.*, 2019. Advance research progresses in aluminium matrixcomposites: Manufacturing & applications. Journal of Materials Research and Technology. 8 (5), 4924-4939. doi:[10.1016/j.jmrt.2019.06.028](https://doi.org/10.1016/j.jmrt.2019.06.028).

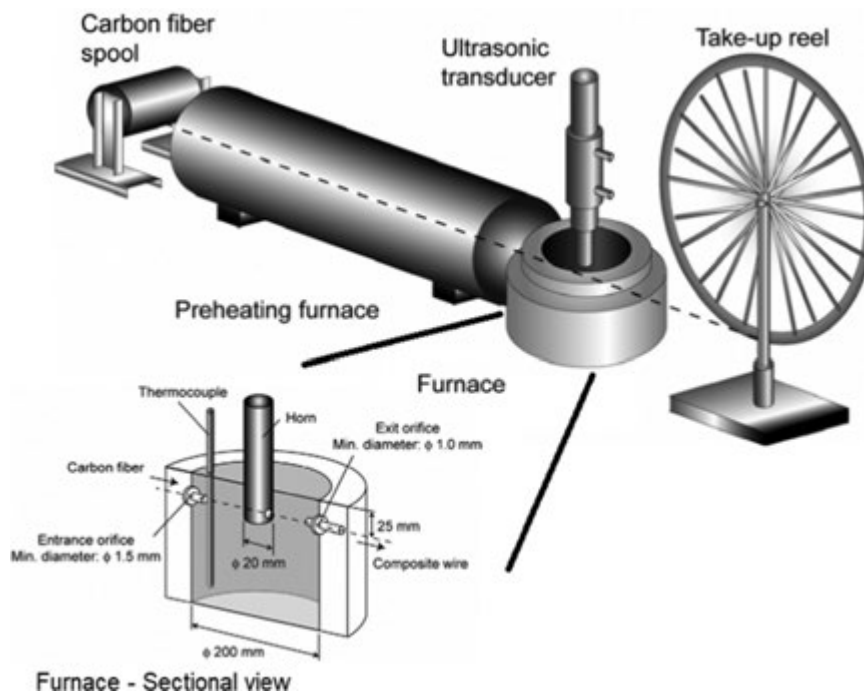


Fig. 7 Ultrasonic infiltration furnace set up. Reproduced from Matsunaga, T., *et al.*, 2007. Fabrication of continuous carbon fiber-reinforced aluminum-magnesium alloy composite wires using ultrasonic infiltration method. Composites Part A: Applied Science and Manufacturing. 38 (8), 1902-1911. doi:[10.1016/j.compositesa.2007.03.007](https://doi.org/10.1016/j.compositesa.2007.03.007).

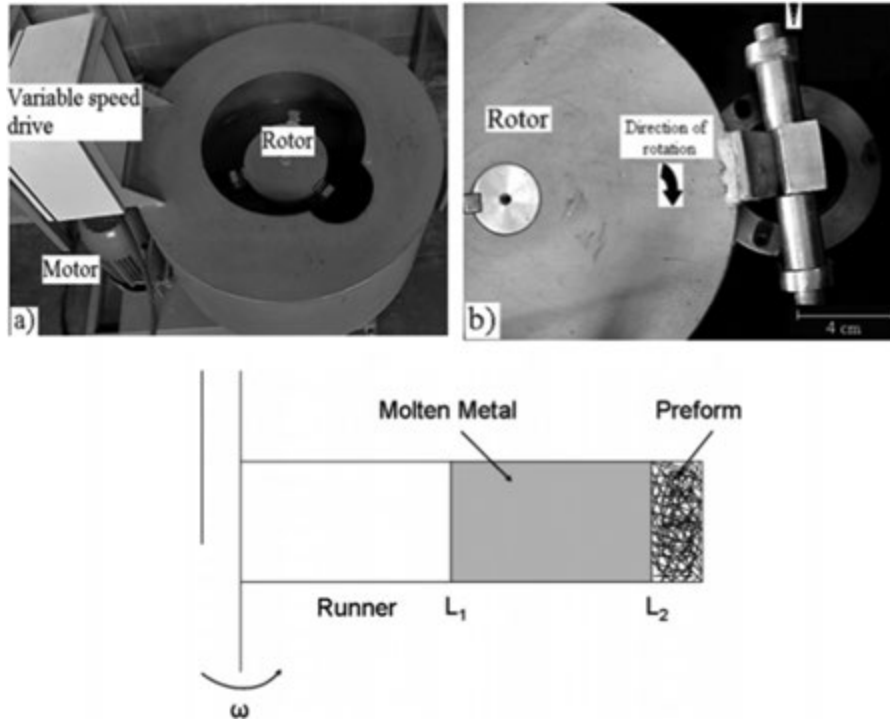


Fig. 8 Centrifugal infiltration setup and principle. From Sánchez, M., Rams, J., Ureña, A., 2010. Fabrication of aluminium composites reinforced with carbon fibres by a centrifugal infiltration process. *Composites Part A: Applied Science and Manufacturing*. 41 (11), 1605-1611. doi:[10.1016/j.compositesa.2010.07.014](https://doi.org/10.1016/j.compositesa.2010.07.014). Sánchez-Martínez, A., *et al.*, 2016. Main process parameters for manufacturing open-cell Zn-22Al-2Cu foams by the centrifugal infiltration route and mechanical properties. *Materials and Design*. 108, 494-500. doi:[10.1016/j.matdes.2016.07.032](https://doi.org/10.1016/j.matdes.2016.07.032).

Centrifugal infiltration:

In this process, the reinforcement is positioned inside a mold with long runners filled with molten metal which infiltrates the preform under large rotational velocities or centrifugal forces which is given by:

$$P_c = \frac{1}{2} \rho \omega^2 (L^2) \quad (1)$$

where, P_c = pressure generated at the preform top surface during the rotation in centrifugal casting, ρ = density of the molten metal, $\omega = 2\pi\Omega/60$ where Ω is rotational speed (rpm), L = molten metal level from the rotational axis (Sánchez *et al.*, 2010; Sánchez-Martínez *et al.*, 2016) (Fig. 8)

Lorentz force infiltration:

It is an infiltration technique in which a high frequency electromagnetic pulse is used to immerse the reinforcement into the molten metal and the interaction of magnetic pulse with eddy current generates Lorentz force to force the liquid metal to enter in reinforcement phase at a very high speed (Andrews and Mortensen, 1991) (Fig. 9).

Squeeze casting:

Squeeze casting infiltration process is one of the widely used fabrication techniques for producing net shape MMCs with control over shapes, chemistry, volume fraction and distribution of reinforcement (Uozumi *et al.*, 2008). In squeeze casting, the molten metal is forced into the preform and a pressure is applied until the solidification is complete. This method can be applied for both the fibers and particles reinforced composites as the prefabricated fiber or particle preforms can be melt infiltrated and solidified under pressure. To avoid damage to the preforms, the melt is first pressed into the preform at low pressure and then the pressure is increased for solidification. Since the melt solidifies under very high pressure, the squeeze cast composites are free from the common casting defects such as porosity and shrinkage cavities. As the duration of the infiltration is relatively short, the squeeze casting method can be applied for reactive materials like magnesium (Jayalakshmi *et al.*, 2006) (Fig. 10).

Based on the mode of pressure application, squeeze casting can be classified into direct and indirect squeeze casting. In direct squeeze casting method, pressure for the infiltration of preforms is applied directly to the melt. However, in indirect squeeze casting, the melt is pressed into the preform through a gate system. Although the tooling is relatively simple for direct squeeze casting, the absence of gate system necessitates accurate determination of the melt volume. Another disadvantage is the presence of oxide residue in the composite which are normally restricted by the gate in the indirect squeeze casting.

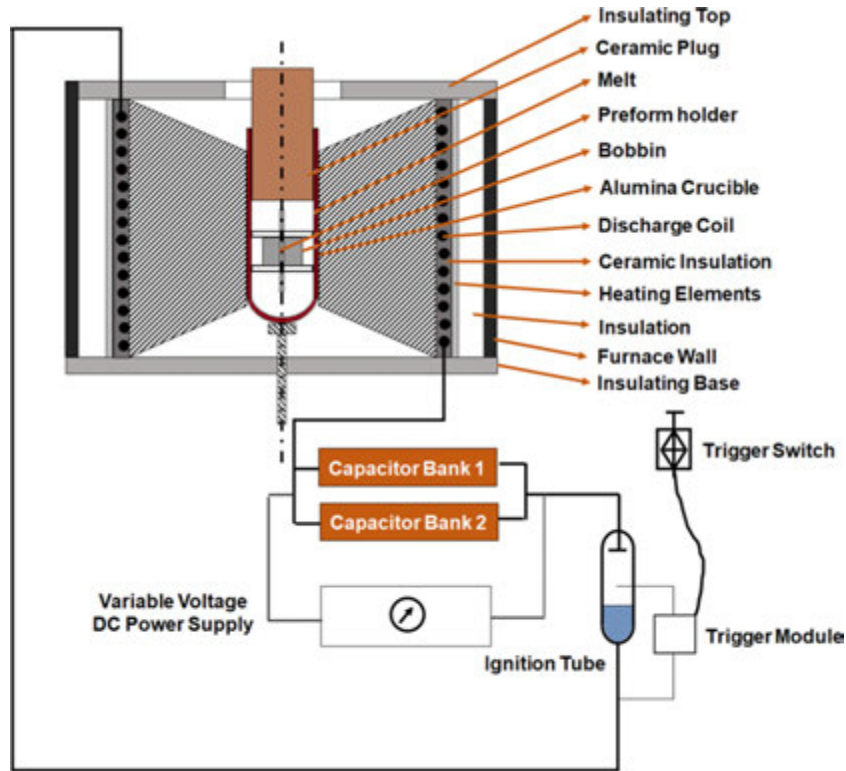


Fig. 9 Lorentz force infiltration setup. Reproduced from Andrews, R.M., Mortensen, A., 1991. Lorentz force infiltration of fibrous preforms. Metallurgical Transactions A.22, 2903–2915. doi:10.1007/BF02650251.

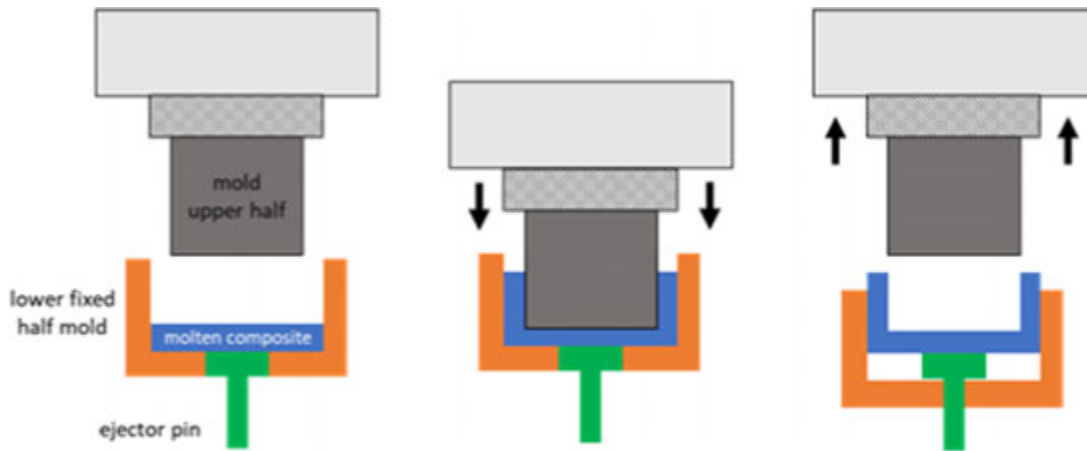


Fig. 10 Squeeze casting. Redrawn from Garg, P., *et al.*, 2019. Advance research progresses in aluminium matrixcomposites: Manufacturing & applications. Journal of Materials Research and Technology. 8 (5), 4924–4939. doi:10.1016/j.jmrt.2019.06.028.

Stir casting

Stir casting or compo-casting is the most common and cost-effective method of producing composite materials (Kainer, 2006; Tzamtzis *et al.*, 2009). In this method, the reinforcement phase (fiber or particles) is mixed with the molten matrix metal by means of mechanical or ultrasonic stirring. The molten composite slurry is then cast by conventional casting methods. The properties of the MMCs produced using stir casting methods will depend on the processing parameters such as temperature of melt, stirring speed, stirring duration, geometry of the stirrer and size of crucible which will affect the distribution of the reinforcements in the matrix. The dispersed phases are also often coated with proper wetting agents to achieve better interfacial bonding with the matrix material and to avoid any unwanted reaction and the dissolution of reinforcement at high temperatures. In case of particulate reinforcement, careful attention must be paid to the dispersion of the particles as they tend to form agglomerates. In general, the

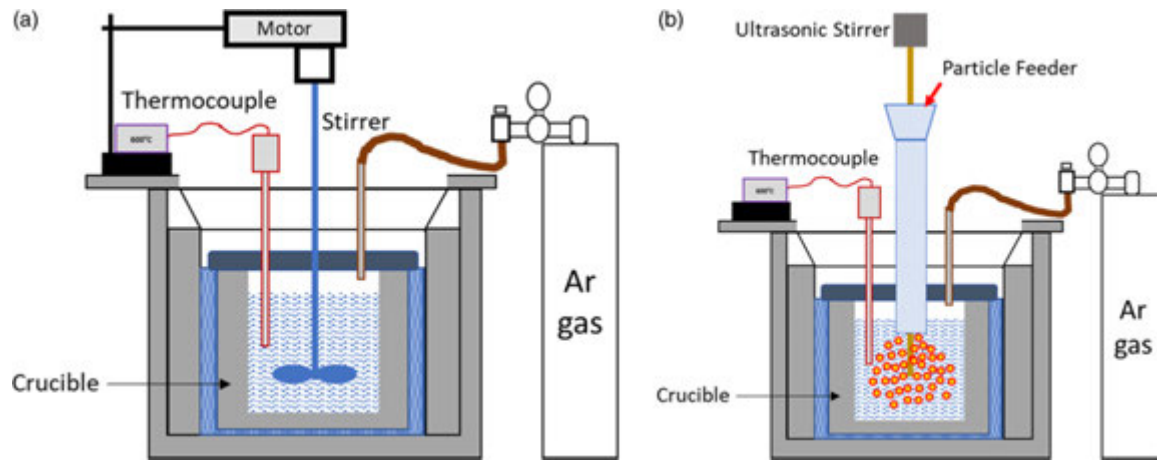


Fig. 11 Schematic of (a) mechanical stir casting and (b) ultrasonic stir casting.

proper selection of processing parameters such as melt temperature, stirring speed, duration, and stirrer geometry, etc., allows the effective dispersion of particles (in the size range 5–100 μm) up to 30% by volume (Fig. 11).

Melt deposition

There are several deposition techniques available to produce metal matrix composites. While deposition methods like immersion and electroplating, chemical vapor deposition (CVD), physical vapor deposition (PVD) are only used for fiber reinforced MMCs, the spray and disintegrated melt deposition methods can be used for both the particle reinforced metal matrix composites (Harrigan, 1998).

Immersion plating:

This method is applicable for continuous fiber reinforcement which are passed through baths of molten metal, slurry, sol, or organometallic precursors.

Electroplating or electrodeposition:

In this method, the matrix metal coating is produced from a solution containing the ion of the desired material in the presence of an electric current. As this process is carried out at moderate temperatures, this method offers less/no damage to the reinforcement fibers. However, processing defects such as poor bonding and porosity are common for MMCs produced using this method. Also, only limited alloy matrices can be processed using this method.

Chemical vapor deposition:

It involves chemical reaction or decomposition of a vaporized component on to the substrate to form a coating. Using this method, amorphous and crystalline (single and polycrystals) coatings of oxide, carbide, nitride, or pure metals can be made. When this method is used to deposit the matrix material on the reinforced preforms, it is called chemical vapor infiltration.

Physical vapor deposition:

This method is highly suitable for producing fiber reinforced metal matrix composites in which the vapors of matrix metal were condensed to create coatings on the reinforcement fibers. The coated fibers are then consolidated by hot pressing or hot isostatic pressing. Based on the vapor generation techniques, the PVD processes can be classified into: (1) evaporation based, (2) sputtering, and (3) ion-plating. While the evaporation PVD methods include techniques based on electron beam/arc evaporation, radiation heating, laser ablation and resistive heating, the sputtering techniques involve vaporization of the coating material from an ionized argon gas molecule via momentum transfer. Similarly, ion plating involves passing the vaporized component through an argon gas glow discharge around the substrate which ionizes and subsequently deposit the vapor onto the substrate.

The primary advantage of PVD is the versatility in the compositions of the coating produced and the superior bonding with the substrate. In addition, there are no chemical reaction by products in these methods. However, the PVD methods are relatively complex and expensive.

Spray deposition:

In spray deposition, reinforcements in the form of particles/whiskers are injected into the spray of molten metal, creating a deposition layer on the substrate (Wood, 1997). The depositions are then densified by suitable post-processing techniques. Similarly, for continuous fiber reinforcements, the molten matrix metal is sprayed onto the fibers with preferred orientation. In this method, fiber alignment can be easily controlled and a relatively faster solidification rates can be achieved.

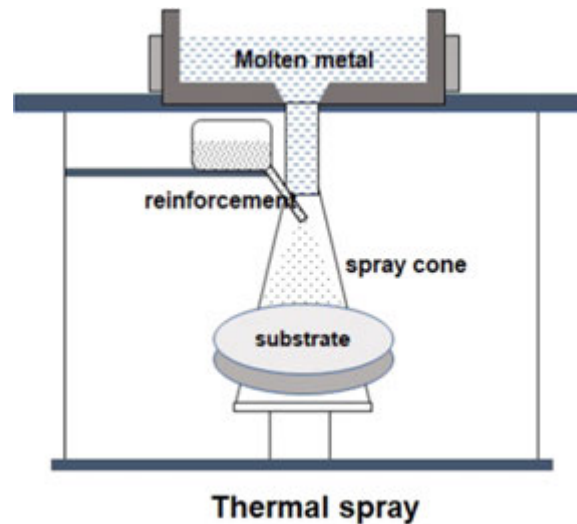


Fig. 12 Spray deposition. Redrawn from Garg, P., *et al.*, 2019. Advance research progresses in aluminium matrixcomposites: Manufacturing & applications. Journal of Materials Research and Technology. 8 (5), 4924–4939. doi:10.1016/j.jmrt.2019.06.028.

It is a promising method for producing particle reinforced MMCs. It involves spray techniques which are used to develop monolithic alloys. Fig. 12 shows an example of the spray forming process in which a spray gun is used to atomize the molten matrix metal into which the reinforcement particles are injected. The resulting metal matrix composite (about 97% dense) is then subjected to scalping, consolidation, and secondary finishing processes to produce wrought composites. To facilitate the efficient transfer of particle reinforcement, an optimum particle size and shape must be maintained.

Disintegrated melt deposition:

Disintegrated melt deposition (DMD) is a unique liquid processing technique which combines the advantages of stir casting and spray processing methods (Gupta *et al.*, 1995) (Fig 13). It involves the vortex mixing of reinforcements and the deposition of molten slurry onto a metallic substrate after disintegration by jets of inert gases. Unlike spray deposition, DMD employs lower impinging velocity to achieve a bulk composite. Hence, it offers the features of (1) fine grain structure and low segregation of reinforcements of spray process and (2) simplicity and cost effectiveness of conventional stir cast foundry process.

Solid State Processing

Some of the widely used solid-state processing methods include (1) powder mixing, (2) mechanical alloying, (3) diffusion bonding, and (4) deformation processing.

Powder consolidation

In this method, the required amounts of matrix alloy and reinforcement powders are mixed to prepare a composite blend which is then cold or hot compacted into a billet. The prepared green billet is then canned, degassed and sintered at temperature closer to the solidus temperature of the matrix alloy (Sankaranarayanan and Gupta, 2015) (Fig. 14).

While this method can be effectively used for particle reinforced aluminum or magnesium composites, cold-pressing and sintering are not preferred in case of long fiber reinforcement which are often damaged under the high pressure. Hence, for long continuous fibers, the fiber tows are first infiltrated by dry matrix powder which is then followed by hot isostatic pressing (Gupta and Sharon, 2010).

Mechanical alloying

Mechanical alloying involves repeated cold welding, fracturing, and re-welding of powder particles in a high energy ball mill (Suryanarayana, 2001). In this process, the frictional heat developed at the particle interface results in the local melting and consolidation of powder particles. The composite powder mixture obtained from ball-milling is then densified using cold or hot-pressing techniques (Sankaranarayanan and Gupta, 2015) (Fig. 15).

Due to the nature of high dislocation densities generated in this method and the homogenous distribution of reinforcing constituents, this method can be effectively applied to develop a range of equilibrium/non-equilibrium alloys and composites with excellent set of properties.

Post-processing (or) sintering of powder compact

Cold compacted billets from the powder mixing and mechanical alloying methods are often heat treated or sintered for better densification and strengthening. It involves heating of the green compact to a temperature closer to the solidus line of the matrix

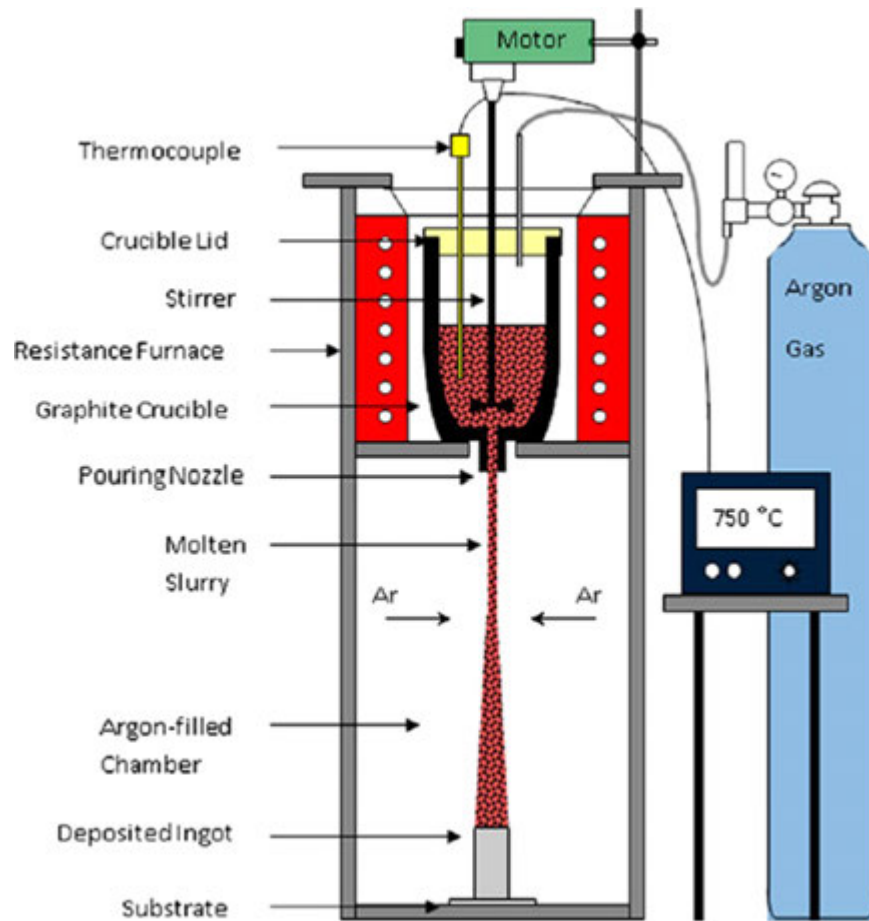


Fig. 13 Disintegrated melt deposition. Reproduced from Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization*.105, 30-46. doi:[10.1016/j.matchar.2015.04.015](https://doi.org/10.1016/j.matchar.2015.04.015).

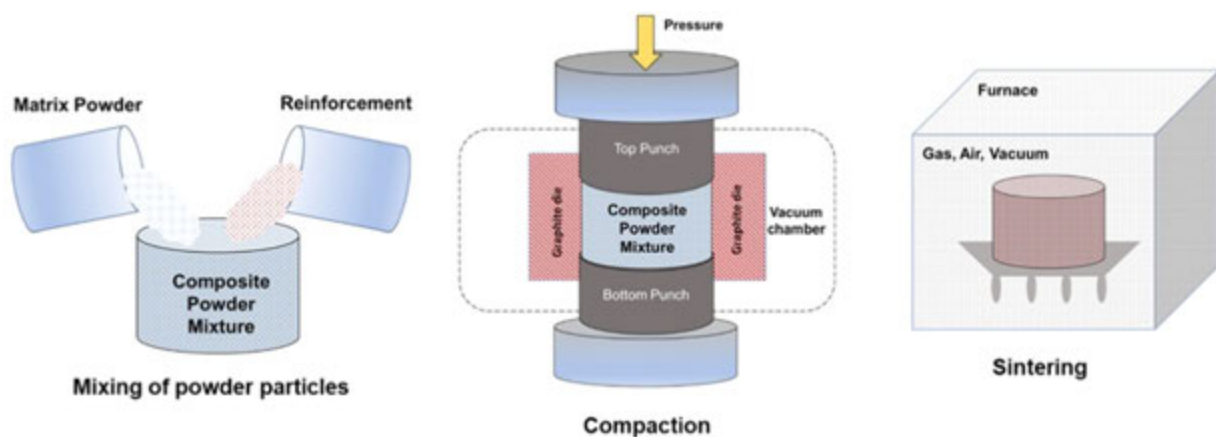


Fig. 14 Powder consolidation.

alloy for a certain period in order to allow atomic diffusion and inter-particle bonding (Padmavathi *et al.*, 2011; Slotwinski *et al.*, 2014). In most cases, the sintering of green powder compact also facilitates the microstructural recrystallization for strengthening alongside densification and removal of residual lubricant (Fig. 16).

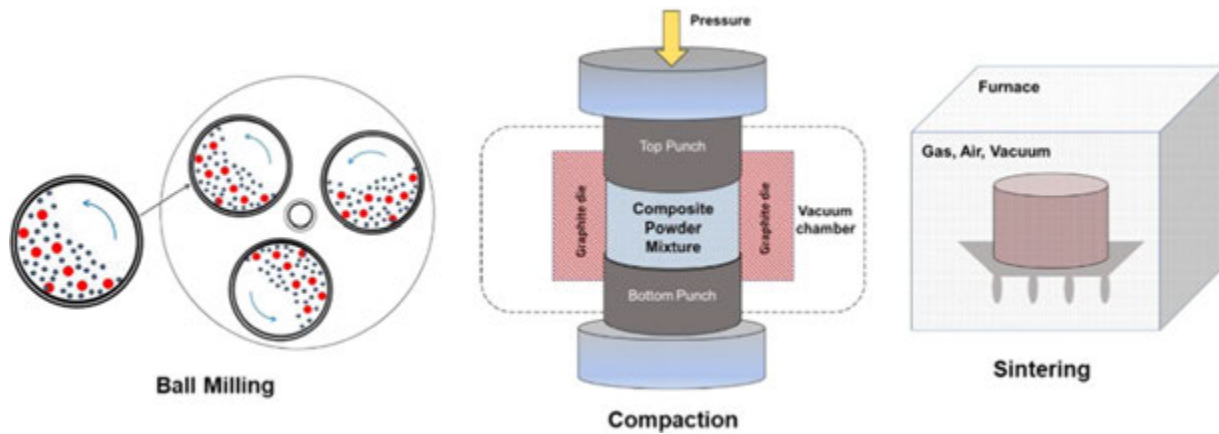


Fig. 15 Schematic showing mechanical alloying.

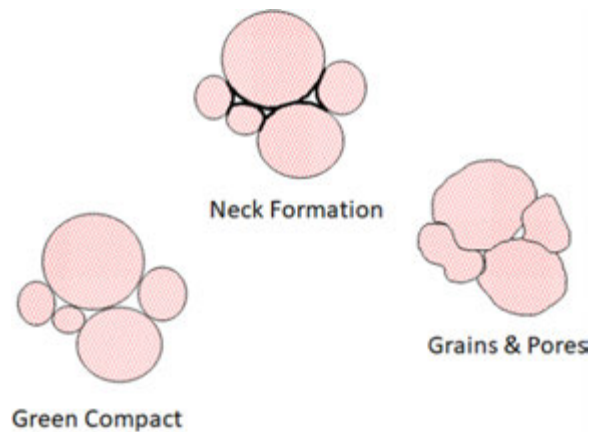


Fig. 16 Stages in sintering: Stage I: Particle bonding in green compact, Stage II: Growth of contact points into 'necks' and Stage III: final microstructure showing grains and pores.

Microwave assisted rapid sintering

Microwave sintering has recently emerged as an energy efficient technique to consolidate powder materials (Wong and Gupta, 2007; Gupta and Eugene, 2011; Padmavathi *et al.*, 2011). While the microwave processing has been largely limited to ceramic materials in the past, recent literatures confirm that the metallic materials can also be densified using the microwaves. However, it should be noted that the microwave heating is fundamentally different compared to conventional heating. In conventional heating, the transfer of heat from the surface to the interior of material takes place by conduction, convection and radiation. However, microwave heating involves the self-heating of material core due to dielectric and magnetic losses resulting from the interaction between the electric and magnetic fields (Fig. 17). Since microwaves exhibit an inverse temperature distribution, the heating by microwaves happens rapidly from the core to the surface and cause a substantial reduction in the processing time by more than 80%. Hybrid microwave sintering utilizing susceptors in recent year has emerged to minimize temperature and microstructural variations across the thickness of samples.

Diffusion bonding

Diffusion bonding is a solid-state technique used to process a wide variety of fiber reinforced MMCs. It involves the interdiffusion of atoms at the mating surface between the matrix and reinforcement to cause chemical/mechanical bonding under the influence of temperature and pressure (Fig. 18). Although the fiber orientation and volume fraction can be effectively controlled, the processing time and cost are relatively high thus limiting its extended application.

Deformation processing

Fabrication methods based on mechanical deformation are highly applicable for metal-metal or layered metal composites. Fig. 19 illustrates the methodology of roll bonding process used to produce sheet metal composite laminates. Here, a two-phase alloy

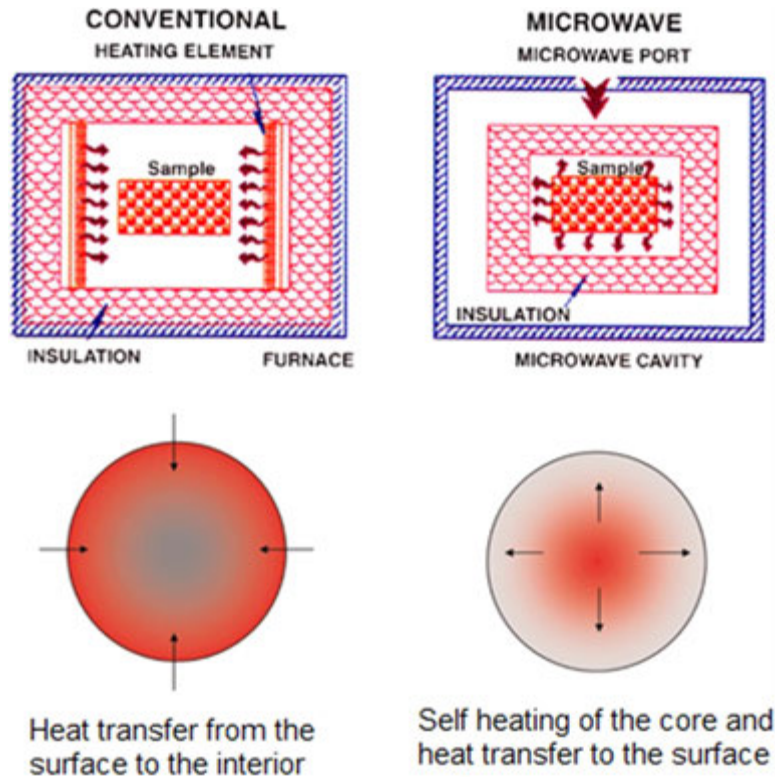


Fig. 17 Schematic of microwave sintering and heat transfer principle. Modified from Penchal Reddy, M., *et al.*, 2016. Microwave rapid sintering of al-metal matrix composites: A review on the effect of reinforcements, microstructure and mechanical properties. Metals. doi:10.3390/met6070143.

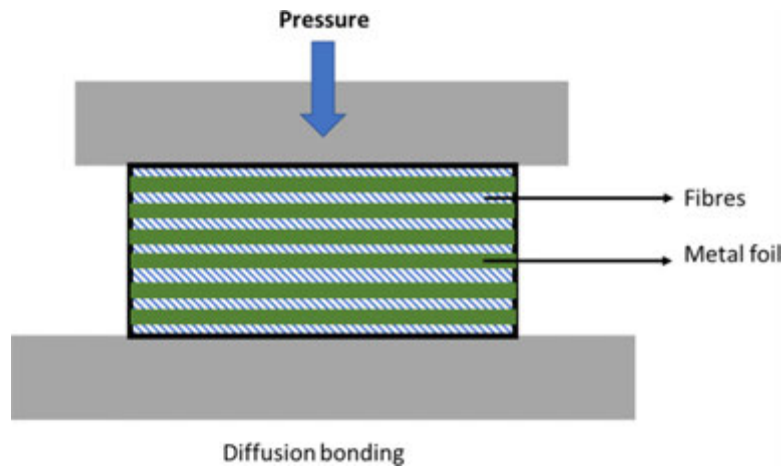


Fig. 18 Schematic showing diffusion bonding process. Redrawn from Garg, P., *et al.*, 2019. Advance research progresses in aluminium matrixcomposites: Manufacturing & applications. Journal of Materials Research and Technology. 8 (5), 4924–4939. doi:10.1016/j.jmrt.2019.06.028.

material is subjected to mechanical deformation causing the minor phase to elongate and become fibrous within the matrix (major phase). However, it should be noted that this method is limited to ductile two-phase materials in which the two phases exhibit similar flow stresses pattern for co-deformation. Further, the deformation processed materials also require post-processing heat treatments to reduce mechanical anisotropy.

In-Situ Processes

In-situ methods include processes based on liquid–gas, liquid–solid, liquid–liquid, and mixed salt reactions in which the chemical reaction between reacting constituents leads to in-situ formation of reinforcement (Harrigan, 1998; Thein *et al.*, 2009; Ghosh *et al.*, 2010;

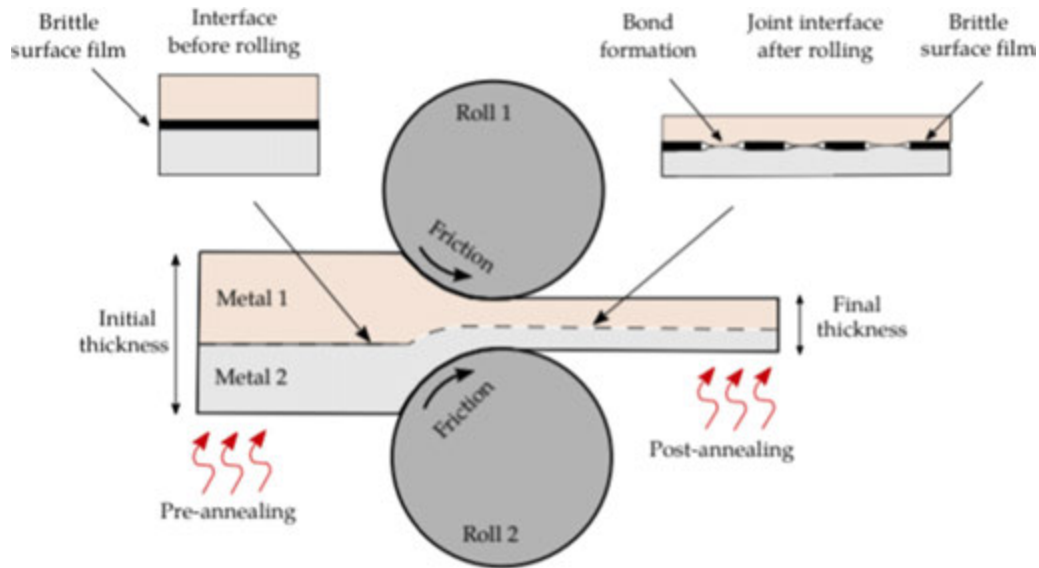


Fig. 19 Roll bonding process for making a laminated MMC. Reproduced from Khaledi, K., *et al.*, 2018. Modeling of joining by plastic deformation using a bonding interface finite element. *International Journal of Solids and Structures*. doi:10.1016/j.ijsolstr.2018.10.014.

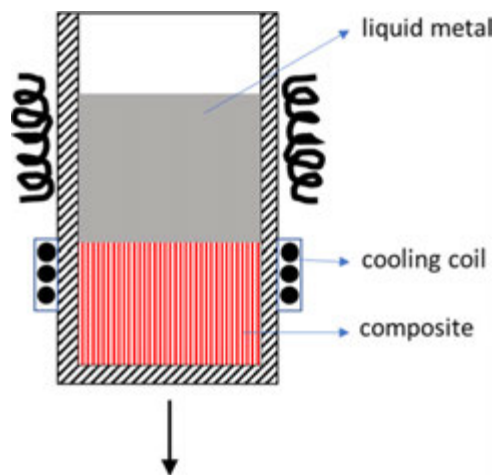


Fig. 20 Self-propagating high temperature synthesis of MMCs. Redrawn from Garg, P., *et al.*, 2019. Advance research progresses in aluminium matrixcomposites: Manufacturing & applications. *Journal of Materials Research and Technology*. 8 (5), 4924–4939. doi:10.1016/j.jmrt.2019.06.028.

Jayalakshmi *et al.*, 2013). Hence, a good understanding of reaction kinetics and thermodynamics is essential in order to obtain the desirable end-products. Generally, the in-situ developed composites exhibit very fine and well dispersed reinforcement phases which are stable and free from surface contaminants and has a coherent interface assisting in stronger bond between the reinforcement and the matrix material.

One of the well-known examples of in-situ methods is the unidirectional solidification of eutectic alloy resulting in the formation and distribution of fibers like phases in the matrix alloy (Livingston, 1974). Sometimes, it is also referred to as self-propagating high temperature synthesis (SHS) when the reinforcing phases are produced by exothermic reaction between the matrix constituents (Subrahmanyam and Vijayakumar, 1992; Mossino, 2004; Xiao *et al.*, 2004) (Fig. 20). In these methods, the characteristics of the reinforcing phases, especially the interfacial compatibility are controlled by the solidification rate which is generally limited to $\sim 1\text{--}5$ cm/h to maintain the temperature gradient for a stable growth front.

Additive Manufacturing

Laser-based additive manufacturing techniques such as selective laser melting and laser deposition were also used to fabricate metal matrix composites based on Al, Ti, and Ni based matrix materials (Gu *et al.*, 2012; Manfredi *et al.*, 2014; Pouzet *et al.*, 2016;

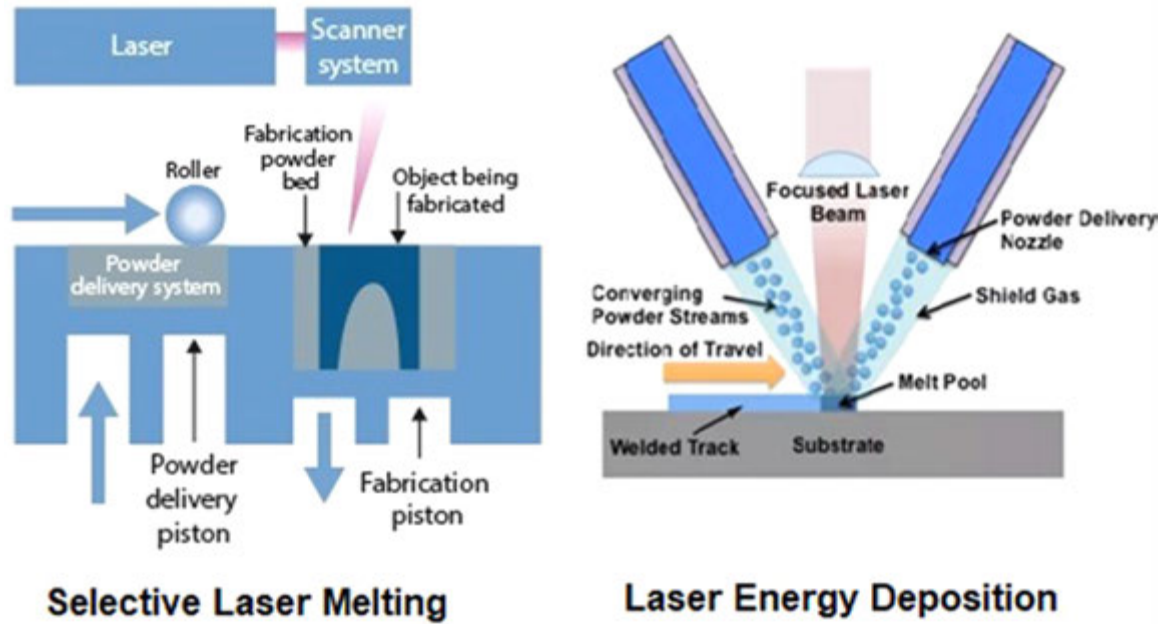


Fig. 21 Schematic of selective laser melting and laser deposition methods. Courtesy Benedyk, J.C., 2018. Additive manufacturing of aluminum alloys: Augmenting or competing with traditional manufacturing? *Light Metal Age*.

Aboulkhair *et al.*, 2019; Behera *et al.*, 2019). These methods involved a high energy laser source to melt and deposit the powder raw materials in a layer-by-layer fashion (Fig. 21). In most cases, the reinforcement phases are often developed in-situ due to the chemical reaction between the powder raw materials (Banerjee *et al.*, 2005; Attar *et al.*, 2014a). On the other hand, the laser processing of ex-situ prepared composite powder mixture was also investigated and it was found that the composite powder preparation plays an important role in determining the end properties of the bulk composite (AlMangour *et al.*, 2016, 2017a,b; Famodimu, 2016).

Properties of MMCs

The end properties of composite materials are controlled by many variables including reinforcement form, volume fraction, geometry, distribution, matrix/reinforcement interface, void content, and manufacturing process. The presence, amount, and distribution of reinforcement influence the dislocation behavior and hence the physical and mechanical properties of the composites. In addition to physical and mechanical properties, the reinforcement also influences other material properties such as the wear resistance and damping capacity. The mechanical properties of MMCs are not only affected by the properties of matrix and reinforcing materials, but also by the interfacial characteristics and it is well established that the weak bonding between them generally worsen the properties of MMCs. The following section will provide an overview of the properties of metal matrix composites.

Volume and Weight Fractions

Based on the rule of mixtures, the properties of a composite material are the volume weighed average of the phases (matrix and dispersed phase) properties. Hence, to estimate the mechanical properties of a composite material, it is important to know the relative proportions of matrix and reinforcement. The proportion can be expressed in terms of volume fraction of weight (or mass) fraction. Weight fractions are commonly used as it is easy to weigh the relative proportions of matrix and reinforcement using an analytical balance. The volume fraction is used in the computation of the properties of the composite, therefore knowing the conversion between weight and volume fraction is essential.

The relationships between the volume fractions and weight fractions can be expressed as:

$$W_m = \frac{\rho_m}{\rho_c} V_m \text{ and } W_R = \frac{\rho_r}{\rho_c} V_r \quad (2)$$

where,

W_m and W_r → weight fraction of matrix and reinforcement materials, respectively,
 V_m and V_r → volume fractions of matrix and reinforcement materials, respectively

ρ_m , ρ_r and $\rho_c \rightarrow$ densities of matrix, reinforcement and the composite, respectively.

Density

The density of metal matrix composite can be calculated using the rule of mixtures as follows:

$$\rho_c = \rho_m V_m + \rho_r V_r \text{ (or) } \rho_c = \frac{1}{\frac{V_m}{\rho_m} + \frac{V_r}{\rho_r}} \quad (3)$$

Coefficient of Thermal Expansion

Based on the rule of the rule of mixtures (Dieter and Bacon, 1988), the thermal expansion coefficient of composite material can be computed as follows:

$$\alpha_c = \alpha_m V_m + \alpha_r V_r \quad (4)$$

where α_c , α_m and α_r refers to the thermal expansion coefficients of the composite, matrix and reinforcement materials, respectively.

For continuous fiber reinforced metal matrix composites, the thermal expansion coefficients along the longitudinal and transverse directions can be calculated as follows:

CTE in longitudinal direction (along the fibers),

$$\alpha_{cl} = \frac{\alpha_m E_m V_m + \alpha_r E_r V_r}{E_m V_m + E_r V_r} \quad (5)$$

CTE in transverse direction (perpendicular to the fibers),

$$\alpha_{ct} = (1 + V_m) \alpha_m + \alpha_r V_r \quad (6)$$

where E_m , E_r are the elastic moduli of the matrix and the fiber reinforcement respectively and v_m refers to the poisson's ratio of the matrix.

Similarly, for particle reinforced MMCs, the coefficient of thermal expansion can also be calculated based on the Turner model (Elomari *et al.*, 1998) as below:

$$\alpha_c = \frac{(\alpha_m V_m K_m + \alpha_r V_r K_r)}{(V_m K_m + V_r K_r)} \quad (7)$$

where K_m and K_r is the bulk modulus of matrix and reinforcement, respectively.

Modulus of Elasticity

The elastic behavior of a composite depends on the type and volume fraction of the reinforcement and it generally improves with the addition of the reinforcement (Dieter and Bacon, 1988):

$$E_C = E_m V_m + E_r V_r \quad (8)$$

Along the transverse direction,

$$E_{ct} = \frac{1}{\left(\frac{V_m}{E_m} + \frac{V_r}{E_r}\right)} \quad (9)$$

For discontinuous fibers and particle (aspect ratio: s) reinforced composites, the elastic modulus can be calculated as follows:

$$E_c = \frac{E_m(1 + 2sqV_r)}{1 - qV_r} \text{ when } q = \frac{\left(\frac{E_r}{E_m} - 1\right)}{\left(\frac{E_r}{E_m} + 2s\right)} \quad (10)$$

Tensile Strength

Metal matrix composites exhibit better strength when compared to their unreinforced matrix metals and the same can be calculated as follows:

$$\sigma_c = \sigma_m + \sqrt{\sum \Delta \sigma_i^2} \quad (11)$$

where σ_c and σ_m refers to the strength of the composite and the matrix respectively and $\Delta \sigma$ refers to the strengthening contribution from various strengthening mechanism as described below:

Load transfer

The transfer of load from relatively soft and compliant matrix material to the hard and strong reinforcement actively contributes towards the strengthening of matrix as proposed in the original and modified shear lag theories (Fukuda and Chou, 1981; Clyne, 1989) as follows:

$$\Delta\sigma_{LT} = V_r \sigma_m \frac{(L+t)AL}{4L} \quad (11a)$$

where σ_m , L and t refers to the matrix yield strength, and reinforcement dimensions in terms of length and thickness, respectively. Hence, for equiaxed particle reinforcements, the strength contribution from load transfer may be expressed simply as $\Delta\sigma_{LT} = 0.5V_r \sigma_m$

Strengthening due to CTE and EM mismatch

The dislocation density in a composite matrix is generally higher due to the thermal stresses caused by the mismatch in CTE ($\Delta\alpha_{CTE}$) and modulus ($\Delta\sigma_{EM}$) values between the matrix and the reinforcement materials (Dieter and Bacon, 1988; Callister and Rethwisch, 2007).

$$\Delta\sigma_{CTE} = \frac{A\Delta\alpha\Delta TV_r}{b d v_m} \quad (11b)$$

$$\Delta\sigma_{EM} = \frac{6V_r}{\pi d} \quad (11c)$$

where A is a geometric constant, $\Delta\alpha$ is the CTE mismatch, ΔT is the temperature difference, b is Burgers vector and d is reinforcement size.

Thermal residual stresses

The strengthening contribution from residual stress due to thermal cycling at high temperatures can be calculated using the following relation (Chawla and Chawla, 2004):

$$\Delta\sigma_{Ts} = \frac{E_r E_m}{E_r V_r + E_m V_m} V_r \Delta\alpha \Delta T \quad (11d)$$

Orowan strengthening

Orowan mechanism applies to dispersion strengthened materials in which the dislocation motion is restricted by presence of reinforcements in the form of fibers or particles which can be expressed as (Dieter and Bacon, 1988; Callister and Rethwisch, 2007):

$$\Delta\sigma_{OR} = \frac{0.13bG}{d_r \left[\left(\frac{1}{2V_r} \right)^{1/3} - 1 \right]} \ln \left(\frac{d}{2b} \right) \quad (11e)$$

where G is the matrix shear modulus.

Grain refinement strengthening

In polycrystalline metals, grain boundaries play an important role in strengthening as they impede the dislocation motion at low temperatures to increase the stress required for continuing the deformation process (Dieter and Bacon, 1988; Callister and Rethwisch, 2007). As the matrix grain size of MMCs is usually smaller than that of the unreinforced counterparts, the greater grain boundary area prevents the dislocations from moving in a continuous slip plane leading to an increase in the yield strength. The Hall–Petch equation relates the yield strength of the material with the average grain size (d) as follows:

$$\Delta\sigma_{HP} = \frac{K_y}{\sqrt{d}} \quad (11f)$$

where K_y is the strengthening coefficient which is a characteristic constant of each material.

In a recent work, Zhang and Chen proposed the following simplified model considering the strengthening mechanisms such as Orowan strengthening mechanism, CTE mismatch effect, and load-bearing effect as follows:

$$\sigma_c = (1 + 0.5V_r) \left(\sigma_m + A + B + \frac{AB}{\sigma_m} \right) \quad (12)$$

$$A = 1.25G_m b \sqrt{\frac{12\Delta\alpha\Delta TV_r}{b d V_m}} \quad (12a)$$

$$B = \frac{0.13G_m b}{d^{1/3} \sqrt{\frac{1}{2}V_r - 1}} \ln \frac{d}{2b} \quad (12b)$$

Application of MMCs

Metal matrix composites are used in a range of applications ranging from aerospace, space, automobile, cutting tools, power transmission, consumer electronics, defense, and sports (Clyne and Withers, 1995; Kainer, 2006).

The enhanced stiffness and strength of the MMCs make them highly suitable for applications in military and commercial aircrafts. For example, the aluminum access doors in the F-16 aircraft have been replaced with SiC particle reinforced MMCs for fatigue life improvement (Hunt, 2001). Similarly, the SiC monofibre reinforced Ti-composites are used to replace the heavier IN718 and stainless-steel components of the F119 engine in F-16 (Warrier, 1995; Doorbar *et al.*, 2009). Some other examples include ~20% lighter airframe of Boeing 787 made of largely carbon fiber composites and the fan-exit guide vane of a Pratt & Whitney engine on a Boeing 777 (Haghshenas, 2016). Recently, structural components for tank armours are also made using BN reinforced steel composites.

Transportation sector has been the prime consumer of MMCs and the applications in this field include drive shafts, engine and brake components. For example, modern sport cars built by Porsche use rotor components made of carbon fiber composites with better specific heat and thermal conductivity (Chawla and Chawla, 2006; Macke *et al.*, 2012). Similarly, Al-Si matrix composites containing Al₂O₃ and carbon with improved wear resistance and ~50% weight savings are used in the cylinder liner of Honda Prelude (Chawla and Chawla, 2006; Nicolais *et al.*, 2012; Macke *et al.*, 2012). Other automotive applications of MMC include piston rings made of short Saffil fiber reinforced Al composites in Toyota car models, connecting rods and drive shafts made of SiC/B₄C particle-reinforced aluminum-matrix composites for structural lightweighting of racing cars, and Duralcan supplied brake rotors of German high-speed train made of SiC particles reinforced AlSi₇Mg composite with ~43% weight savings (Cayron, 2001; Chawla and Chawla, 2006; Nicolais *et al.*, 2012; Macke *et al.*, 2012). Similarly, the brake calipers and pushrods supplied by 3M also offer upto 50% weight saving potential (Hunt Warren and Miracle, 2001).

Another common example of MMCs is the lightweight bicycle frame made using aluminium/titanium matrix composites and carbon fibers. Some other sporting applications include fishing rods, bicycle frames, golf club heads, and tennis/squash rackets (Koczak *et al.*, 1993). MMCs reinforced with carbide and nitride particles are also widely used as cutting tool materials (Ozben *et al.*, 2008).

In electronics applications, MMCs are used in the new generation advanced integrated circuits to overcome heat dissipation and thermal fatigue concerns. Dymalloy, a metal matrix composite containing diamond particles in copper-silver alloy matrix with very high thermal conductivity and adjustable thermal expansion coefficients are used as substrates for high power, high density multi-chip modules in microelectronics (Davidson *et al.*, 1995; Kerns *et al.*, 1996). Similarly, continuous Al₂O₃ fiber reinforced Al MMCs with adjustable CTE are used as electrical conductors for power transmission (Huda *et al.*, 1995).

Challenges and Recommendations

In this article, the fundamentals of metal matrix composites are discussed in terms of their classification, processing, and properties. Their applications in key engineering sectors such as automobile, aerospace, and electronics are also briefly reviewed. As of now, the research works on MMCs largely focussed on lightweight metals such as Al, Mg, Ti for automotive and aerospace applications. However, materials like copper, tin, and iron also offer exceptional promise in electronics and tooling applications.

The lightweight MMCs with desirable properties such as high specific modulus, better thermal stability, and wear/abrasion resistance have emerged as the front runner for weight critical applications. However, there are substantial technical and infrastructure challenges which need to be addressed in order to effectively use them as alternatives to conventional materials. Some of those key challenges are discussed below.

Metal matrix composites require reinforcements in the form of defect free fibers and particles which are often expensive. Hence, the economic production of low cost and high strength reinforcement would be timely. In this regard, the effective utilization of eco-friendly and recycled materials as reinforcement is also recommended.

Fabrication techniques suitable for MMCs are highly complicated when compared to conventional materials. Hence, any research advancements related to the development of user-friendly and environmentally conscious fabrication methods that are capable of fabricating defect free composites would be timely given that these materials are often more brittle than their unreinforced matrix counterpart.

With respect to properties, poor ductility and toughness are the major limitations of MMCs. Although the recent research works have identified some of the possible ways to overcome these limitations through nanoscale reinforcements, thermal treatments, and secondary processing, systematic fundamental investigations linking the process-structure-property relationships are required for commercialization. Similarly, issues concerning the operations such as joining, machining and recycling also require due attention.

References

- Aboulkhair, N.T., *et al.*, 2019. 3D printing of aluminium alloys: Additive manufacturing of aluminium alloys using selective laser melting. *Progress in Materials Science* 106, 100578. doi:10.1016/j.pmatsci.2019.100578.
- Adabisi, A.A., Maleque, M.A., Rahman, M.M., 2011. Metal matrix composite brake rotors: Historical development and product life cycle analysis. *International Journal of Automotive and Mechanical Engineering* 4, 471–480. doi:10.15282/ijame.4.2011.8.0038.

- AlMangour, B., Grzesiak, D., Yang, J.M., 2016. Nanocrystalline TiC-reinforced H13 steel matrix nanocomposites fabricated by selective laser melting. *Materials and Design* 96, 150–161. doi:10.1016/j.matdes.2016.02.022.
- AlMangour, B., Grzesiak, D., Yang, J.M., 2017a. Selective laser melting of TiB₂/316L stainless steel composites: The roles of powder preparation and hot isostatic pressing post-treatment. *Powder Technology* 309, 37–48. doi:10.1016/j.powtec.2016.12.073.
- AlMangour, B., Grzesiak, D., Yang, J.M., 2017b. Selective laser melting of TiB₂/H13 steel nanocomposites: influence of hot isostatic pressing post-treatment. *Journal of Materials Processing Technology* 244, 344–353. doi:10.1016/j.jmatprotec.2017.01.019.
- Altinkok, N., Demir, A., Ozsert, I., 2003. Processing of Al₂O₃/SiC ceramic cake preforms and their liquid Al metal infiltration. *Composites Part A: Applied Science and Manufacturing* 34 (7), 577–582. doi:10.1016/S1359-835X(03)00125-8.
- Andrews, R.M., Mortensen, A., 1991. Lorentz force infiltration of fibrous preforms. *Metallurgical Transactions A* 22, 2903–2915. doi:10.1007/BF02650251.
- Ashby, M.F., 2005. *Materials Selection in Mechanical Design*, third ed. doi:10.1016/B978-1-85617-663-7.00001-1.
- Attar, H., et al., 2014a. Selective laser melting of in situ titanium-titanium boride composites: Processing, microstructure and mechanical properties. *Acta Materialia* 76, 13–22. doi:10.1016/j.actamat.2014.05.022.
- Bakshi, S.R., Lahiri, D., Agarwal, A., 2010. Carbon nanotube reinforced metal matrix composites – A review. *International Materials Reviews* 55, 41–64. doi:10.1179/095066009X125725-30170543.
- Banerjee, R., et al., 2005. Nanoscale TiB precipitates in laser deposited Ti-matrix composites. *Scripta Materialia* 53 (12), 1433–1437. doi:10.1016/j.scriptamat.2005.08.014.
- Barrett, T., 2017. The Future of Metal Is in Matrix Composites. Available at: <https://www.machinedesign.com/materials/article/21835569/the-future-of-metal-is-in-matrix-composites>.
- Behera, M.P., Dougherty, T., Singamneni, S., 2019. Conventional and additive manufacturing with metal matrix composites: A perspective. *Procedia Manufacturing* 30, 159–166. doi:10.1016/j.promfg.2019.02.023.
- Bhat, A., et al., 2011. Carbon nanotube reinforced Cu-10Sn alloy composites: Mechanical and thermal properties. *Materials Science and Engineering A* 528, 22–23. doi:10.1016/j.msea.2011.05.038.
- Callister, W., Rethwisch, D., 2007. *Materials science and engineering: An introduction*. *Materials Science and Engineering*. doi:10.1016/0025-5416(87)90343-0.
- Casati, R., Vedani, M., 2014. Metal matrix composites reinforced by nano-particles – A review. *Metals* 4 (1), 65–83. doi:10.3390/met4010065.
- Cayron, C., 2001. TEM study of interfacial reactions and precipitation mechanisms in Al₂O₃ short fiber or high volume fraction SiC particle reinforced Al-4Cu-1Mg-0.5Ag squeeze-cast composites. *EMPA Activities, Empa-Berichte* 250.
- Chawla, K.K., Chawla, N., 2004. *Metal-Matrix Composites*. 1. *Material Science and Technology*. pp. 1–25. doi:10.1016/B978-0-08-050073-7.50011-7.
- Chawla, N., Chawla, K.K., 2006. Metal-matrix composites in ground transportation. *JOM* 58, 67–70. doi:10.1007/s11837-006-0231-5.
- Clyne, T.W., 1989. A simple development of the shear lag theory appropriate for composites with a relatively small modulus mismatch. *Materials Science and Engineering A* 122 (2), 183–192. doi:10.1016/0921-5093(89)90629-1.
- Clyne, T.W., Withers, P.J., 1995. *An Introduction to Metal Matrix Composites*. Cambridge University.
- Cook, A.J., Werner, P.S., 1991. Pressure infiltration casting of metal matrix composites. *Materials Science and Engineering A* 144 (1–2), 189–206. doi:10.1016/0921-5093(91)90225-C.
- Daoud, A., 2004. Wear performance of 2014 Al alloy reinforced with continuous carbon fibers manufactured by gas pressure infiltration. *Materials Letters* 58 (25), 3206–3213. doi:10.1016/j.matlet.2004.06.012.
- Davidson, H.L., et al., 1995. Copper-diamond composite substrates for electronic components. *Proceedings – Electronic Components and Technology Conference*. doi:10.1109/ectc.1995.515335.
- Dieter, G.E., Bacon, D., 1988. *Mechanical metallurgy SI metric edition*. *Journal of the Franklin Institute*. doi:10.1016/S0016-0032(62)91145-6.
- Doorbar, P., Dixon, M., Chatterjee, A., 2009. Aero-engine titanium from alloys to composites. *Materials Science Forum* 618–619, 127–134. doi:10.4028/www.scientific.net/MSF.618-619.127.
- Elomari, S., et al., 1998. Thermal expansion behavior of particulate metal-matrix composites. *Composites Science and Technology* 58 (3–4), 369–376. doi:10.1016/s0266-3538(97)00124-3.
- Esawi, A.M.K., Farag, M.M., 2007. Carbon nanotube reinforced composites: Potential and current challenges. *Materials and Design* 28 (9), 2394–2401. doi:10.1016/j.matdes.2006.09.022.
- Famodimu, O.H., 2016. *Additive Manufacturing of Aluminium-Metal Matrix Composite Developed Through Mechanical Alloying*. PhD Thesis: University of Wolverhampton. Available at: <http://hdl.handle.net/2436/620337>.
- Ferguson, J.B., Schultz, B.F., Rohatgi, P.K., 2014. Self-healing metals and metal matrix composites. *JOM* 66, 866–871. doi:10.1007/s11837-014-0912-4.
- Fukuda, H., Chou, T.W., 1981. An advanced shear-lag model applicable to discontinuous fiber composites. *Journal of Composite Materials* 15 (1), 79–91. doi:10.1177/002199838101500107.
- Garg, P., et al., 2019. Advance research progresses in aluminium matrix composites: Manufacturing & applications. *Journal of Materials Research and Technology* 8 (5), 4924–4939. doi:10.1016/j.jmrt.2019.06.028.
- Ghosh, S.K., Saha, P., Kishore, S., 2010. Influence of size and volume fraction of SiC particulates on properties of ex situ reinforced Al-4.5Cu-3Mg metal matrix composite prepared by direct metal laser sintering process. *Materials Science and Engineering A* 527 (18–19), 4694–4701. doi:10.1016/j.msea.2010.03.108.
- Goh, C.S., et al., 2006a. Development of novel carbon nanotube reinforced magnesium nanocomposites using the powder metallurgy technique. *Nanotechnology* 17 (1), 7–12. doi:10.1088/0957-4484/17/1/002.
- Goh, C.S., et al., 2006b. Simultaneous enhancement in strength and ductility by reinforcing magnesium with carbon nanotubes. *Materials Science and Engineering A* 423 (1–2), 153–156. doi:10.1016/j.msea.2005.10.071.
- Gu, D.D., et al., 2012. Laser additive manufacturing of metallic components: Materials, processes and mechanisms. *International Materials Reviews* 57 (3), 133–164. doi:10.1179/1743280411Y.0000000014.
- Gupta, M., Eugene, W.W.L., 2011. *Microwaves and metals*. *Microwaves and Metals*. doi:10.1002/9780470822746.
- Gupta, M., Lai, M.O., Soo, C.Y., 1995. Processing-microstructure-mechanical properties of an Al-Cu/SiC metal matrix composite synthesized using disintegrated melt deposition technique. *Materials Research Bulletin* 30 (12), 1525–1534. doi:10.1016/0025-5408(95)00141-7.
- Gupta, M., Sharon, N.M.L., 2010. *Magnesium, Magnesium Alloys, and Magnesium Composites*. Wiley. doi:10.1002/9780470905098.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46. doi:10.1016/j.matchar.2015.04.015.
- Haghshenas, M., 2016. *Metal-matrix composites*. Reference Module in Materials Science and Materials Engineering Elsevier. doi:10.1016/B978-0-12-803581-8.03950-3.
- Harrigan, W.C., 1998. Commercial processing of metal matrix composites. *Materials Science and Engineering A* 244 (1), 75–79. doi:10.1016/s0921-5093(97)00828-9.
- Huda, M.D., Hashmi, M.S.J., El-Baradie, M.A., 1995. MMCs: Materials, manufacturing and mechanical properties. *Metal Matrix Composites* 104, 37–64. doi:10.4028/www.scientific.net/KEM.104-107.37.
- Hunt, W.H., 2001. Metal matrix composites: Applications. *Encyclopedia of Materials: Science and Technology*. 5442–5446. doi:10.1016/B0-08-043152-6/00950-5.
- Hunt Warren, H.J., Miracle, D.B., 2001. Automotive applications of metal-matrix composites. *Composites* 21, 1029–1032. doi:10.31399/asm.hb.v21.a0003484.
- Jayalakshmi, S., et al., 2006. Properties of squeeze cast Mg-6Zn-3Cu alloy and its sapphire alumina short fibre reinforced composites. *Journal of Materials Science* 41, 3743–3752. doi:10.1007/s10853-005-4484-0.

- Jayalakshmi, S., *et al.*, 2013. Microstructure and mechanical properties of Mg-Al alloys with in situ Al_3C_3 phase synthesised by CO_2 incorporation during liquid state processing. *International Journal of Microstructure and Materials Properties* 8 (4–5), doi:10.1504/IJMP.2013.057066.
- Jayalakshmi, S., Gupta, M., 2015. Light metal matrix composites. *Metallic Amorphous Alloy Reinforcements*. doi:10.1007/978-3-319-15016-1_2.
- Jayalakshmi, S., Singh, R., Gupta, M., 2018. Metallic glasses as potential reinforcements in Al and Mg matrices: A review. *Technologies* 6 (2), 40. doi:10.3390/technologies6020040.
- Kainer, K.U., 2006. Basics of metal matrix composites. *Combination of Materials for Light Metal Matrix Composites*. doi:10.1002/3527608117.ch1.
- Kerns, J.A., *et al.*, 1996. Dymalloy: A composite substrate for high power density electronic components. *International Journal of Microcircuits and Electronic Packaging*.
- Koczak, M.J., *et al.*, 1993. Metal-matrix composites for ground vehicle, aerospace, and industrial applications. *Fundamentals of Metal-Matrix Composites*. 297–326. doi:10.1016/B978-0-08-052371-2.50020-1.
- Livingston, J.D., 1974. Unidirectional solidification of eutectic and eutectoid alloys. *Journal of Crystal Growth* 24–25, 94–101. doi:10.1016/0022-0248(74)90285-1.
- Macke, A., Schultz, B.F., Rohatgi, P., 2012. Metal matrix: Composites offer the automotive industry an opportunity to reduce vehicle weight, improve performance. *Advanced Materials and Processes* 170 (3), 5.
- Manfredi, D., *et al.*, 2014. Additive manufacturing of Al alloys and aluminium matrix composites (AMCs). *Light Metal Alloys Applications*, IntechOpen. doi:10.5772/58534.
- Matsunaga, T., *et al.*, 2007. Fabrication of continuous carbon fiber-reinforced aluminum-magnesium alloy composite wires using ultrasonic infiltration method. *Composites Part A: Applied Science and Manufacturing* 38 (8), 1902–1911. doi:10.1016/j.compositesa.2007.03.007.
- Mossino, P., 2004. Some aspects in self-propagating high-temperature synthesis. *Ceramics International* 30 (3), 311–332. doi:10.1016/S0272-8842(03)00119-6.
- Neubauer, E., *et al.*, 2010. Potential and challenges of metal-matrix-composites reinforced with carbon nanofibers and carbon nanotubes. *Composites Science and Technology* 70 (16), 2228–2236. doi:10.1016/j.compscitech.2010.09.003.
- Nicolais, L., Chawla, K.K., Chawla, N., 2012. Automotive composites. In: *Wiley Encyclopedia of Composites*, pp. 1–6. doi:10.1002/9781118097298.weoc012.
- Ozben, T., Kilickap, E., Çakir, O., 2008. Investigation of mechanical and machinability properties of SiC particle reinforced Al-MMC. *Journal of Materials Processing Technology* 198 (1–3), 220–225. doi:10.1016/j.jmatprotec.2007.06.082.
- Padmavathi, C., Upadhyaya, A., Agrawal, D., 2011. Effect of microwave and conventional heating on sintering behavior and properties of Al-Mg-Si-Cu alloy. *Materials Chemistry and Physics* 130 (1–2), 449–457. doi:10.1016/j.matchemphys.2011.07.008.
- Popov, V.N., 2004. Carbon nanotubes: Properties and application. *Materials Science and Engineering R: Reports* 43 (3), 61–102. doi:10.1016/j.mser.2003.10.001.
- Pouzet, S., *et al.*, 2016. Additive layer manufacturing of titanium matrix composites using the direct metal deposition laser process. *Materials Science and Engineering A* 677, 171–181. doi:10.1016/j.msea.2016.09.002.
- Rohatgi, P.K., 2014. Al-shape memory alloy self-healing metal matrix composite. *Materials Science and Engineering A* 619, 73–76. doi:10.1016/j.msea.2014.09.050.
- Saboori, A., *et al.*, 2018. An overview of key challenges in the fabrication of metal matrix nanocomposites reinforced by graphene nanoplatelets. *Metals* 8 (3), 172. doi:10.3390/met8030172.
- Sánchez-Martínez, A., *et al.*, 2016. Main process parameters for manufacturing open-cell Zn-22Al-2Cu foams by the centrifugal infiltration route and mechanical properties. *Materials and Design* 108, 494–500. doi:10.1016/j.matdes.2016.07.032.
- Sánchez, M., Rams, J., Ureña, A., 2010. Fabrication of aluminium composites reinforced with carbon fibres by a centrifugal infiltration process. *Composites Part A: Applied Science and Manufacturing* 41 (11), 1605–1611. doi:10.1016/j.compositesa.2010.07.014.
- Sankaranarayanan, S., Gupta, M., 2015. Review on mechanical properties of magnesium (nano)composites developed using energy efficient microwaves. *Powder Metallurgy* 58 (3), doi:10.1179/1743290115Y.0000000009.
- Slotwinski, J.A., *et al.*, 2014. Characterization of metal powders used for additive manufacturing. *Journal of Research of the National Institute of Standards and Technology* 119, 460–493. doi:10.6028/jres.119.018.
- Subrahmanyam, J., Vijayakumar, M., 1992. Self-propagating high-temperature synthesis. *Journal of Materials Science* 27, 6249–6273. doi:10.1007/BF00576271.
- Suryanarayana, C., 2001. Mechanical alloying and milling. *Progress in Materials Science* 46 (1–2), 1–184. doi:10.1016/S0079-6425(99)00010-9.
- Thein, M.A., Lu, L., Lai, M.O., 2009. Effect of milling and reinforcement on mechanical properties of nanostructured magnesium composite. *Journal of Materials Processing Technology* 209 (9), 4439–4443. doi:10.1016/j.jmatprotec.2008.10.044.
- Tzamtzis, S., *et al.*, 2009. Processing of advanced Al/SiC particulate metal matrix composites under intensive shearing – A novel Rheo-process. *Composites Part A: Applied Science and Manufacturing* 40 (2), 144–151. doi:10.1016/j.compositesa.2008.10.017.
- Uozumi, H., *et al.*, 2008. Fabrication process of carbon nanotube/light metal matrix composites by squeeze casting. *Materials Science and Engineering A* 495 (1–2), 282–287. doi:10.1016/j.msea.2007.11.088.
- Sijpkens, T., Vergouwen, P., 2004. Composite materials for structural landing gear components. In: *ERF 2004*, 38. Available at: https://dspace-erf.nl.nl/xmlui/bitstream/handle/20.500.11881/282/38_sijpkens.pdf?sequence=1&isAllowed=y.
- Warrier, S.G., 1995. Developments in the processing of titanium matrix composites. *Key Engineering Materials* 104–107, 475–482. doi:10.4028/www.scientific.net/kem.104-107.475.
- Wong, W.L.E., Gupta, M., 2007. Development of Mg/Cu nanocomposites using microwave assisted rapid sintering. *Composites Science and Technology* 67 (7–8), 1541–1552. doi:10.1016/j.compscitech.2006.07.015.
- Wood, J., 1997. Spray atomisation and deposition. *Surface Engineering*. doi:10.1179/sur.1997.13.1.28.
- Xiao, G., *et al.*, 2004. Dissolution-precipitation mechanism of self-propagating high-temperature synthesis of TiC-Ni cermet. *Materials Science and Engineering A* 14 (6), 568–572. doi:10.1016/j.msea.2004.04.052.

An Insight Into Metal Matrix Composites With Micron Size Reinforcement

Arsha Antony Geetha, Madhusoodhanan Geethakumari Akhil, and Thazhavilai Ponnu Devaraj Rajan, Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India and Academy of Scientific and Innovative Research, Ghaziabad, New Delhi, India

Ballambettu Chandrasekhara Pai, Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composites constitute a class of materials, which make a major industrial impact in fields as diverse as aerospace, automotive and electronics. These composites are made up of a metal matrix packed with particles having very different physical and mechanical properties from those of the matrix. MMCs are attractive due to their cost-effectiveness, isotropic properties, and their ability to be processed using similar technology used for monolithic materials. They can provide significantly enhanced properties like higher strength, stiffness and weight savings in comparison to conventional monolithic materials. The micron sized particle reinforced metal matrix composites are widely used in manufacturing sector due to light-weight, superior strength-to-weight ratio, better fracture toughness, improved fatigue, and tensile property, enhanced corrosion resistance to harsh environment. This article provides an overview of the different types of micron sized reinforcing elements used during the synthesis of MMCs (Jawalkar *et al.*, 2017; Clyne and Withers, 1995; Miracle, 2005). Reinforcement selection criteria include density, melting temperature, elastic modulus, tensile strength, thermal stability, coefficient of thermal expansion, size, compatibility with matrix material, and cost (Clyne and Withers, 1995).

Processing Methods

The production methods can be categorized into two major groups: ex situ and in situ. The first synthesis route consists of adding micro-reinforcements to the liquid or powdered metal, while in situ processes refer to those methods leading to the generation of compounds by reaction during processing. Several methods have been developed for ex situ synthesis of MMCs. In particular, the processing methods such as liquid and powder metallurgy were successfully employed. The processing methods utilized to manufacture particulate reinforced MMCs can be grouped depending different processing methods, accordingly the processes can be classified into three categories: (1) liquid phase processes, (2) solid state processes, and (3) two phase (solid-liquid) processes. In liquid phase processes, the ceramic particulates are incorporated into a molten metallic matrix using various proprietary techniques, followed by mixing and casting of the resulting MMC. In melt infiltration processes, a molten alloy is introduced into a porous ceramic preform, utilizing either inert gas or a mechanical device as a pressurizing medium. Solid phase process variably involves the blending of rapidly solidified powders with particulates, platelets or whiskers. In solid-phase processing, the temperature of the matrix during processing rarely exceeds the solidus temperature. This involves blending a matrix, in powder form with a reinforcing phase, under elevated temperatures and pressures. Semi-solid processes involve mixing the reinforcing phases under thermodynamic conditions such that the matrix contains both solid and liquid.

Strengthening Mechanisms

The strengthening mechanisms are divided into (1) Load transfer from the matrix to the hard reinforcements in MMC, (2) The coefficient of thermal expansion mismatch between matrix and the reinforcement particles, (3) Orowan Strengthening mechanisms in reinforced MMCs, (4) Hall-Petch strengthening mechanisms in reinforced MMCs, (5) Elastic modulus mismatch between matrix and reinforcement particles. Deformation mechanisms involve initial accommodation of applied load by slip or shear band formation followed by load transfer among reinforcements and the matrix. Plastic deformation during processing introduces dislocations which might form substructures that could control the flow stress of the metal-ceramic material. These dislocations may be immobilized by the ceramic particulates and thus be retained in the matrix.

The strengthening mechanisms in metal matrix composites have been related to a high dislocation density in the matrix originating from differential thermal contraction, geometrical constraints and plastic deformation during processing. In addition, stress and strain distributions and possible particle fracture or debonding has effects on properties. Among different shapes, a certain shape of reinforcement particle provided better tensile properties for MMCs and, within each shape category, composites with smaller particle size and higher particle content also showed better properties. It was also found that when the reinforcement content was low the effects of shape and size of the particles were negligible. It was noted that the strength and fatigue life increased with the decrease in particle size and increase in volume fraction (Basak *et al.*, 2019; Taya, 1991; Paknia *et al.*, 2016; Wu and Lavernia, 1992).

Table 1 Physical and mechanical properties of potential reinforcements used in MMCs

Properties	Silicon carbide (SiC)	Alumina (Al ₂ O ₃)	Boron carbide (B ₄ C)	Graphite	Titanium boride (TiB ₂)
Density (gm/cm ³)	3.21	3.89	2.52	1.3–1.95	4.58
Melting point (°C)	2830	2072	2350	3600	3230
Thermal conductivity (W/m K)	120–170	35	30–42	25–470	26
Coefficient of Thermal Expansion (10 ⁻⁶ /°C)	4	8.4	5	8.2	8
Hardness (Kg/mm ²)	2800	1440	2900–3580	33.2	2753.23
Tensile Strength (MPa)	1625	240	569	76	373.6

Types of Reinforcement

Metal matrices are most often based on aluminum, magnesium, copper, and steel have successfully been reinforced with various particles and fibers. Although metallic particles are used in some composites, particles of interest here are primarily ceramic, often made from the lighter elements like SiC, Al₂O₃, B₄C, TiB₂ and TiC. **Table 1** shows the physical and mechanical properties of potential reinforcements used in MMCs. Graphite has also been added to aluminum as a dry lubricant and as a chip-breaking phase in machining but has the disadvantage of being weak, resulting in composites with poor mechanical properties. Material behavior of MMCs depends on the type of reinforcement therefore the understanding of relationship between the strengthening behavior and microstructure is a critical issue in developing metal matrix composites. Different organic, inorganic, industrial and agricultural waste which can be used for reinforcement in the metal matrix is highlighted with their feasible applications. Reinforcing elements such as AlN, CeO₂, GNP, Gr, Cu, TiC, TiN, TiB₂, TaC, SiC, Si₃N₄, ZrO₂, ZnO, ZrB₂, WS₂, etc., were widely used to modify the matrix material as per the requirement and use of the process (Bhoi *et al.*, 2020; Kumar *et al.*, 2010).

Silicon Carbide (SiC)

The SiC particles are the most common discontinuous reinforcements in metal matrix composites for its low cost and readily availability. But still gives the composite high strength and elastic modulus. **Fig. 1(a)** shows the Scanning Electron microscopy images of SiC particles and **Fig. 1(b)** shows the microstructure of aluminum 356–15% SiC-infiltrated composite. The improved wear resistance is often the primary feature as well. In the same way as in the case of continuous SiC fibers the possibility of chemical reactions limits the high temperature applications and may cause problems in production. Silicon Carbide (SiC) and silicon fibers are mainly used in aluminum, magnesium, and copper-matrix composites. Most studies concentrated on composite tensile properties, in particular, the stiffness, strength, and ductility at ambient and elevated temperatures. An increasing trend of hardness and impact strength with increase in weight percentage of SiC has been observed (Karvanis *et al.*, 2016). Microstructure shows the uniform distribution of SiC particles in the matrix resulted due to the good quality preform used and the effective penetration of the liquid metal even in minute voids of the preform. **Table 2** shows the Physio-mechanical properties of aluminum metal matrix composites reinforced with SiC. It is shown that the mechanical properties are increasing with increase in silicon carbide content (**Fig. 2**).

The tribological properties of the material are very important. Incorporation of hard second phase particles in the matrix to produce MMCs has also been reported to be more beneficial and economical (Gül *et al.*, 2012). **Fig. 2** shows Microstructure of aluminum 356 – 50% SiC squeeze infiltrated composite (Ozden *et al.*, 2007). Hardness of the matrix alloy improved significantly by adding SiC particles, while density of the composite also increased almost linearly with the weight fraction of particles (Sahin, 2003; Knowles *et al.*, 2014; Chawla, 2012).

Alumina and Aluminosilicate

The alumina-reinforced metal matrix composites find wide application next to silicon carbide-reinforced composites in the areas of automotive and aerospace industries. These composites possess high elevated-temperature strength, wear resistance, damping properties, electrical conductivity, thermal conductivity and coefficient of thermal expansion. The alumina can be in the form of particulates, whiskers and fibers. There is effects on Al₂O₃ particle content and size of particle on the mechanical properties of the composites such as hardness and tensile strength. This trend is due to an increase in the proportion of the hard Al₂O₃ particulates in the composites, which increases the composites resistance to indentation in comparison to the monolithic alloy (Yan *et al.*, 2008). **Fig. 3** shows the optical microstructure of Al6061-aluminosilicate composite reinforced with 15 vol% of fiber by squeeze infiltration processing. Uniform dispersion of aluminosilicate fibers in the matrix is observed without the formation of porosities and cracks owing to the solidification of the composite (Manu *et al.*, 2016).

Alumino Silicate and Silica

Fig. 4(a) shows the SEM photomicrographs of surface treated micro silica particles and **Fig. 4(b)** microstructure of squeeze cast hypoeutectic micro silica-A356 aluminum alloy in as cast conditions. Microsilica is an artificially synthesized ceramic particle

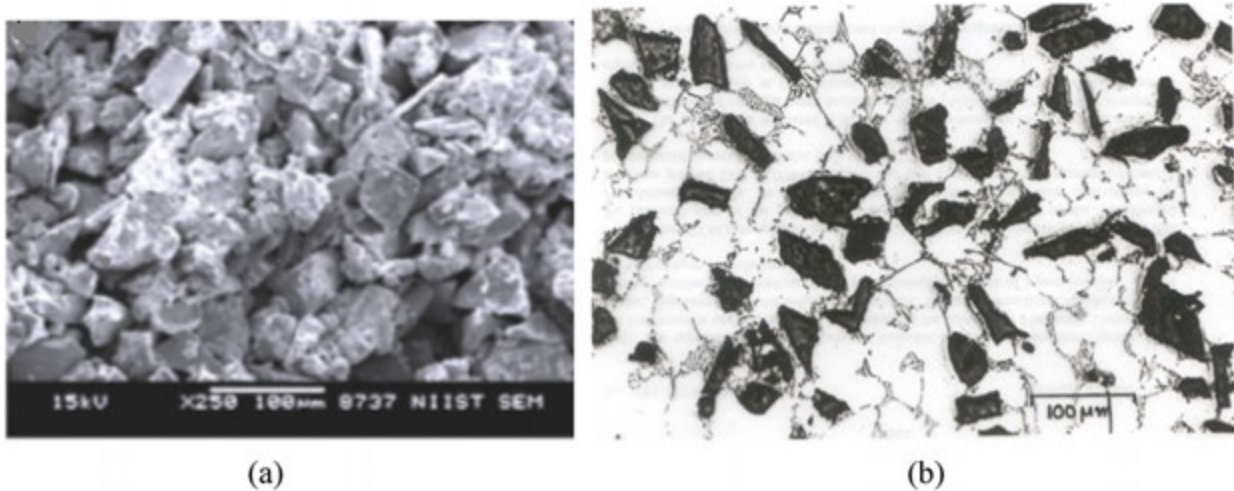


Fig. 1 Scanning Electron microscopy images of (a) SiC particles (b) Stir cast Al 356%–15%SiC Composite.

Table 2 Physio-mechanical properties of aluminum metal matrix composites reinforced with silicon carbide

Material	Density (gm/cm ³)	Hardness (HRB)	Yield strength (MPa)	Impact Strength (J)
Al(AA 6351)	2.69	40	106	4
Al - 4 SiC	2.71	51	125	5
Al - 8 SiC	2.73	56	141	8
Al - 12 SiC	2.75	60	163	11
Al - 16 SiC	2.77	62	175	12
Al - 20 SiC	2.79	65	186	15

Note: Mohanavel, V., Rajan, K., Kumar, S.S., Udishkumar, S., Jayasekar, C., 2018. Effect of silicon carbide reinforcement on mechanical and physical properties of aluminum matrix composites. Materials Today: Proceedings 5, 2938–2944.

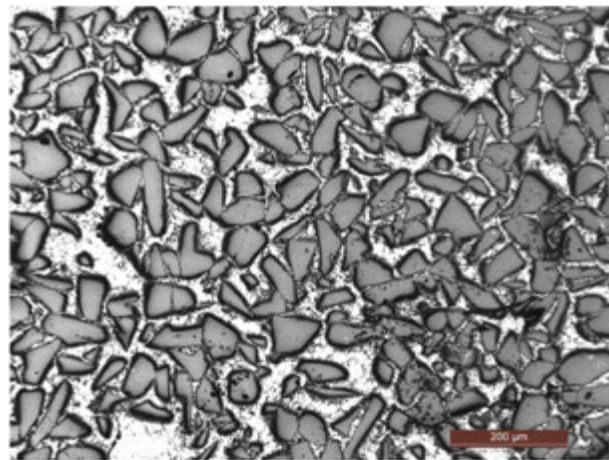


Fig. 2 Microstructure of aluminum 356%–50% SiC squeeze infiltrated composite.

which is widely used as filler in polymer composites. Micro silica stands out as one of the attractive reinforcement with its distinct advantages like low density coupled with thermal stability as well as other properties that stand equal to other commercial reinforcements. Microsilica ceramic particles are fine in size, semi-transparent, white-colored and high-strength microspheres typically used to improve hardness and abrasion resistant coatings. microsilica particles made of alkali alumino silicate ceramic particles. Composites exhibit a remarkable wear resistance with decreased wear rates at an increased sliding velocity due to the formation of tribolayer containing oxygen and iron on the pin surface and abrasive wear mechanism is observed in the material.

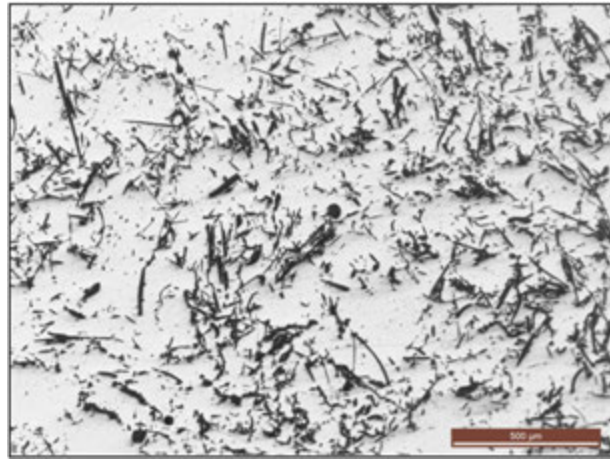


Fig. 3 The optical microstructure of Al6061-aluminosilicate composite reinforced with 15 vol% of fiber by squeeze infiltration processed. Reproduced from Manu, K.S., Rajan, T., Pai, B., 2016. Structure and properties of squeeze infiltrated zirconia grade-aluminosilicate short fiber reinforced aluminum composites. *Journal of Alloys and Compounds* 688, 489–499.

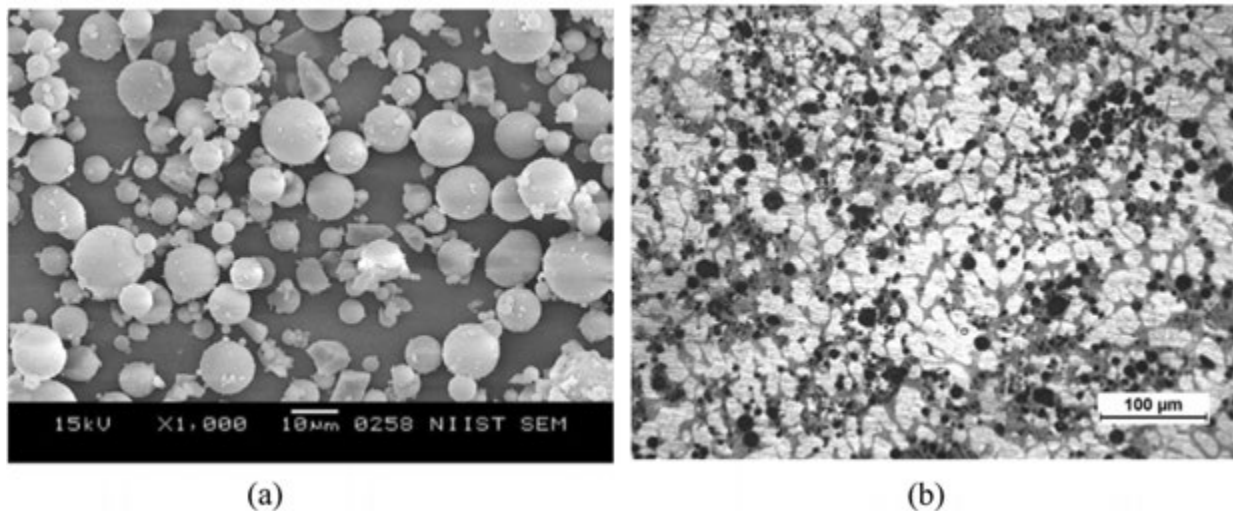


Fig. 4 (a) SEM photomicrographs of surface treated micro silica particles, (b) microstructure of squeeze cast hypoeutectic micro silica-A356 aluminum alloy in as cast conditions. Reproduced from Sree Manu, K., Rahul, P., Ajay Raag, L., *et al.*, 2015. Development of Al 319-micro silica metallic composite by squeeze infiltration technique. *Materials Science Forum*, 489–492.

Carbon

Carbon is one of the predominant reinforcements used in the fabrication of aluminum matrix composites. These composites find wide applications in aerospace, defense and electrical applications due to their high specific strength, high-temperature properties and excellent thermal and electrical conductivities. Carbon is reinforced in various forms namely graphite particles, carbon short and continuous fibers, fullerene, carbon nanotubes and graphene. **Fig. 5(a)** shows the SEM morphologies of graphite flakes and the **Fig. 5(b)** graphite infiltrated A356 aluminum composite.

Carbon is a covalently bonded high melting-point solid that is characterized by closed stable electron configuration and high-strength interatomic bonds. Considerable differences exist in the wetting of carbon by liquid metals ([Asthana, 1998a](#); [Rajan *et al.*, 1998](#)) The potential low cost of the constituent materials also suggests that the graphite MMCs may have an economic advantage over other high-performance composite systems. The presence of graphite particles in the matrix alloys increases their seizure resistance and enables them to run under boundary lubrication without failure. Carbon-fiber composites can be produced with matrices of aluminum. Aluminum reacts with carbon to form the carbide Al_4C_3 , which results in poor composite properties when it appears along the fiber/matrix interface. This reaction can be sufficiently controlled during processing to produce material with

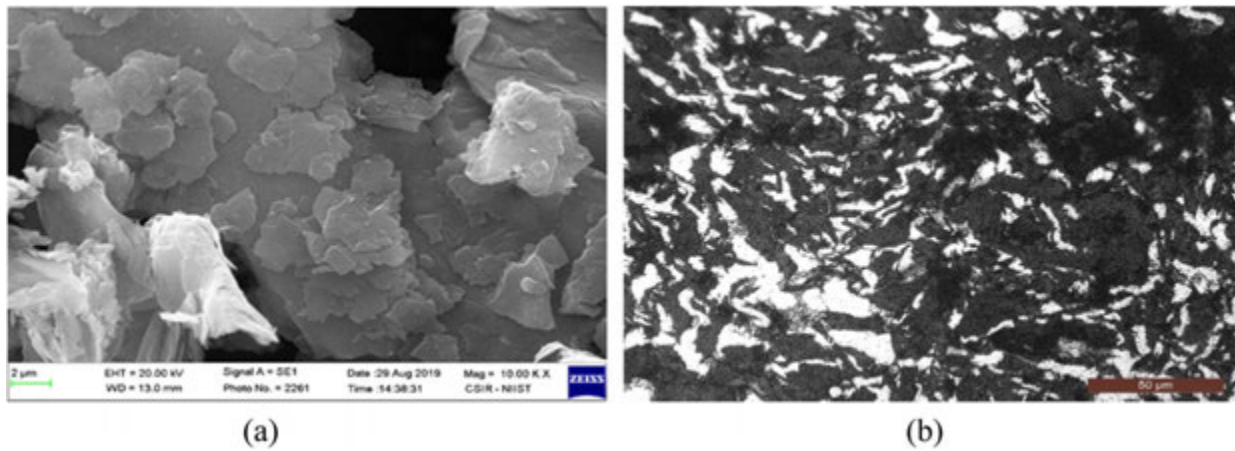


Fig. 5 (a) SEM morphologies of graphite flakes, (b): Optical micrographs of graphite infiltrated A356 aluminum composite. Reproduced from Akhil, M., Arsha, A., Manoj, V., *et al.*, 2020. Squeeze infiltration processing and structural characteristics of lightweight aluminum-carbon metal matrix composites. Transactions of the Indian National Academy of Engineering, 1–8.

Table 3 Tribological properties of aluminum graphite composites

Material	Hardness (BHN)	Wear rate ($\times 10^{-3} \text{ mm}^3/\text{m}$)	Coefficient of friction μ
Al 6061	63	41	0.91
Al 6061/3 Gr	61	78	0.73
Al 6061/5 Gr	59	83	0.65
Al 6061/9 Gr	55	91	0.6
Al6061/13 Gr	83	101	0.56

Note: Mahdavi, S., Akhlaghi, F., 2011. Effect of the graphite content on the tribological behavior of Al/Gr and Al/30SiC/Gr composites processed by in situ powder metallurgy (IPM) method. Tribology Letters 44, 1–12. Peng, X., Huang, Y., Sun, X., Han, X., Fan, R., 2019. Effect of chromium coated carbon fiber on the thermal and mechanical properties of Cr@Gf/Cr@CF/Al composites. Journal of Materials Science: Materials in Electronics 30, 7226–7233.

attractive longitudinal tensile strength and modulus. **Table 3** shows the properties of aluminum graphite composites by powder metallurgy. The specific modulus of 30 vol% graphite aluminum composite fabricated into structural shapes is three times those of ultrahigh strength aluminum, titanium, and steel alloys, whereas the specific strength is comparable. At 50 vol% fibers, the graphite-aluminum will have a specific modulus four times and a specific strength twice that of structural alloys. However, specific strength alone cannot justify the use of graphite-aluminum composite structures since there are other advanced systems that have equally high specific strengths. Copper-graphite and silver-graphite composites have found applications in electrical brushes and contact strips. Aluminum-graphite composites have been successfully tested as materials for bearings, pistons, and liners in engines and electromechanical machinery and their use resulted in improvements in performance and sometimes reduction in cost (Rohatgi *et al.*, 1993). **Table 4** shows the physical properties of aluminum-graphite composite processed by powder metallurgy technique using pure aluminum as matrix and natural flaky graphite (graphitization degree 98%) as the reinforcement. Density and CTE decreases, while thermal conductivity increases with increase in graphite addition. The composites find potential application in thermal management of electronic and computer systems.

Fig. 6 shows the scanning electron microscopy image of carbon fiber and **Fig. 7** shows the optical microstructures of (1) Carbon fiber fabric/Al 6061 infiltrated composite and (2) cross section of the infiltrated composite. Carbon fibers, however, are inherently weak perpendicular to the fiber axis. Properties of carbon fiber reinforced composites along essentially all directions other than the fiber axis, and also in compression along the fibers, are therefore not very attractive compared to achievements with a strongly bonded ceramic fiber in terms of both modulus and strength. Carbon fibers also conduct electricity and there is galvanic coupling between fiber and matrix. Corrosion of carbon fiber reinforced aluminum or magnesium in wet or moist environments is therefore often very severe. For the reinforcement of aluminum, carbon fibers thus have both advantages and disadvantages compared with ceramic fibers.

Fly Ash

Fly ash particles are one of the potential discontinuous dispersoids used in metal matrix composites. They are low-cost and low-density reinforcement available in large quantities as a left-over by-product from thermal power plants. There are two types of fly ash, specifically, precipitator (solid particle) and cenosphere (hollow particle). The major chemical constituents of fly ash are SiO_2 ,

Table 4 Physical properties of aluminum graphite composite

Material composition	Density (g/cm ³)	Thermal conductivity (W/m-K)	CTE (ppm/K)
Aluminum	2.70	225	24
Al - 10% Graphite	2.65	305	16
Al - 20% Graphite	2.60	396	15
Al - 30% Graphite	2.56	430	13
Al - 40% Graphite	2.50	481	12
Al - 50% Graphite	2.45	523	11
Al - 60% Graphite	2.41	555	10.5
Al - 70% Graphite	2.36	690	10.2
Al - 80% Graphite	2.30	720	10
Al - 90% Graphite	2.27	750	9

Note: Chen, J., Huang, I., 2013. Thermal properties of aluminum-graphite composites by powder metallurgy. Composites Part B: Engineering 44, 98–703.

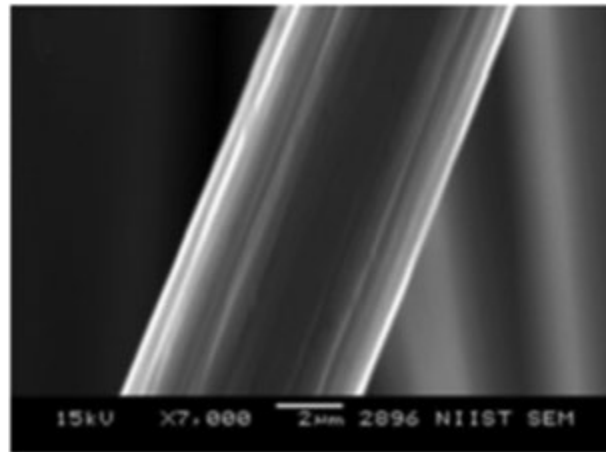
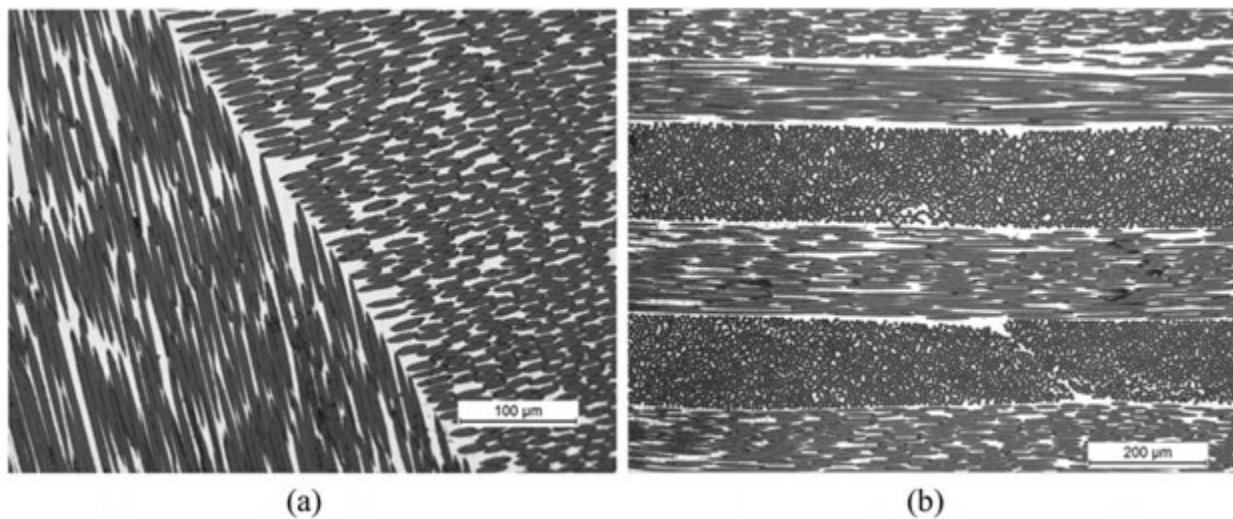

Fig. 6 Scanning electron microscope of Carbon fiber.


Fig. 7 Optical microstructures of (a) carbon fiber fabric/Al 6061 infiltrated composite and (b) cross section of the infiltrated composite. Reproduced from Manu, K.S., Raag, L.A., Rajan, T., *et al.*, 2019. Self-lubricating bidirectional carbon fiber reinforced smart aluminum composites by squeeze infiltration process. Journal of Materials Science & Technology 35, 2559–2569.

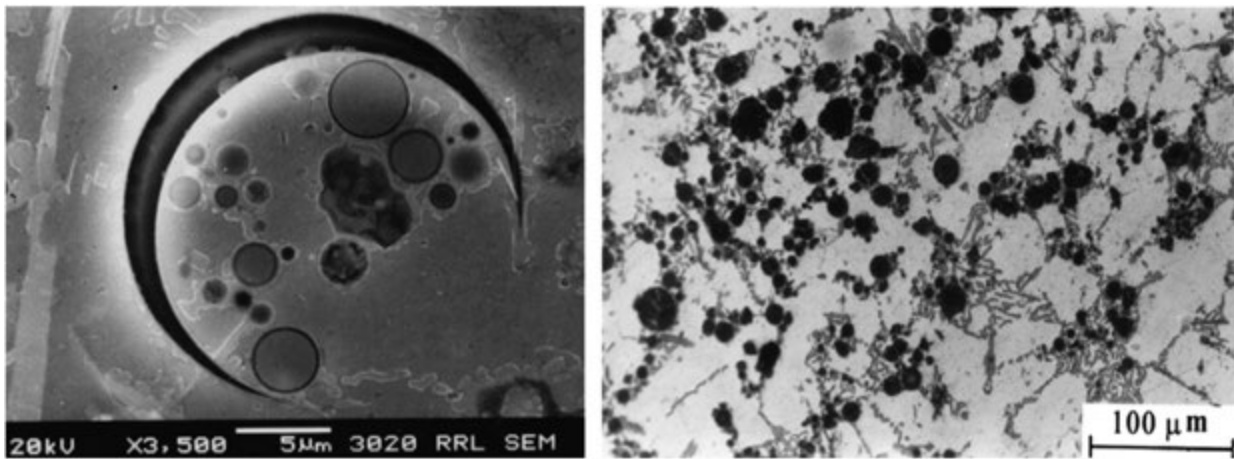


Fig. 8 Optical photomicrographs of Al(356)–15% fly ash composite processed by modified compo-casting followed by squeeze casting. Reproduced from Rajan, T., Pillai, R., Pai, B., 1998. Reinforcement coatings and interfaces in aluminum metal matrix composites. *Journal of materials science* 33, 3491–3503.

Al_2O_3 , Fe_2O_3 and CaO . The fly ash constitutes the alumino silicate glasses containing quartz, mullite, hematite, magnetite, ferrite, spinel, anhydride and alumina. They improve the wear resistance, damping properties, hardness and stiffness and reduce the density of Al alloys.

Fig. 8 shows the optical photomicrographs of A 356–15% fly ash composite processed by modified compo-casting followed by squeeze casting. A linear decrease in the density and ultimate tensile strength and a linear increase in electrical resistivity of Al–12Si–fly ash composites have been observed with increasing dispersoid content. Studies on AK12($\text{AlSi}_{12}\text{CuNiMg}$)/9% Fly ash composites have shown that squeeze casting is more advantageous than gravity casting for obtaining high structural integrity with minimum porosity and these composites show enhanced pitting corrosion than the matrix alloy (Bienia *et al.*, 2003). The average tensile strength in T6 condition for the alloy are 287 and composite is 193 MPa. The reduction in tensile strength in fly ash composites is due to particle fracture and interfacial bonding which is showing in **Table 5**. 12-vol% fly ash reinforced composites exhibit lowest Tensile strength. This low UTS in 12-vol% fly ash reinforced composites is due to the presence of porosity and the formation of second phase particles in the matrix and at particle/matrix interfaces (Surappa, 2008; Ling *et al.*, 2019). Earlier studies on aluminum fly ash composites have also shown the reduction in tensile values for the composites compared to the matrix alloy. **Table 6** shows the density, hardness and tribological properties of Aluminum 2024 Fly Ash Composite. Density values are decreasing with increasing fly Ash content. Also there is an improvement on wear resistance of the composite.

Boron Carbide

Boron carbide (B_4C) is the third hardest material after diamond and cubic boron nitride, which possesses low density, high degree of chemical inertness, high temperature stability, and excellent thermoelectric properties. The atomic structure of boron carbide is rather unique. This unusual structure and bonding is responsible for the excellent thermo-mechanical properties of boron carbide, thus making it a good substitute for many applications (Rajan *et al.*, 1998). Dispersion of B_4C and its interfacial stability is a major issue during its processing (Mahesh *et al.*, 2011).

Fig. 9 shows the SEM micrographs B_4C particles and **Fig. 10** shows the optical micrograph of Al 6061- B_4C particles. This investigation is on the synthesis of B_4C -reinforced 6061 aluminum matrix composite by liquid–metal stir-casting technique under optimized conditions after solving the issues related to the processing, and evaluation of the structural, mechanical, and interfacial characteristics. Interfacial characterization of the composite and the extracted B_4C particles from the matrix has shown the presence of interfacial reaction products such as AlB_2 , Al_3BC , AlB_{12} , and AlB_{10} (Mahesh *et al.*, 2011).

In situ Composites

In situ metal matrix composites refers to the composite in which the reinforcements are formed in situ by exothermal reactions between elements and compounds. Using this approach, MMCs with a wide range of matrix materials including aluminum, titanium, copper, nickel and iron, and second-phase particles including borides, carbides, nitrides, oxides and their mixtures have been produced. Because of the formation of ultrafine and stable ceramic reinforcements, the in situ MMCs are found to exhibit excellent mechanical properties. Compared to the conventional MMCs produced by ex situ methods, the in situ MMCs exhibit the following advantages (1) the in situ formed reinforcements are thermodynamically stable at the matrix, leading to less degradation in elevated-temperature services. (2) The reinforcement matrix interfaces are clean, resulting in a strong interfacial bonding. (3) The in situ formed reinforcing particles are finer in size and their distribution in the matrix is more uniform resulting better

Table 5 Tensile and compression properties of the Aluminum fly ash composites

Material	Tension	Compression	% elongation in tension
A 356	165	458	24
A 356%–6% fly ash	194	548	21
A 356%–12% fly ash	145	427	13

Note: Surappa, M., 2008. Synthesis of fly ash particle reinforced A356 Al composites and their characterization. Materials Science and Engineering: A, 480, 117–124.

Table 6 Properties of aluminum 2024 fly ash composite

Composition	Density (gm/cc)	Rockwell Hardness Number	Wear (Material loss in gms at 30 N load)
Al 2024	2.78	75.00	0.012
Al – 2% Fly Ash	2.74	77.23	0.011
Al – 4% Fly Ash	2.63	79.55	0.009
Al – 6% Fly Ash	2.55	84.50	0.008
Al – 8% Fly Ash	2.49	89.33	0.006
Al – 10% Fly Ash	2.41	93.00	0.004

Note: Subrahmanyam, B.V., Krishna, S.V.G., Pornima, Ch.L., Rao, A.S., 2018. Evaluation of the Mechanical Properties on Aluminum Alloy 2024-Fly Ash Metal Matrix Composite. International Journal of Advanced Mechanical Engineering 8 (1), 1–11. ISSN 2250–3234.

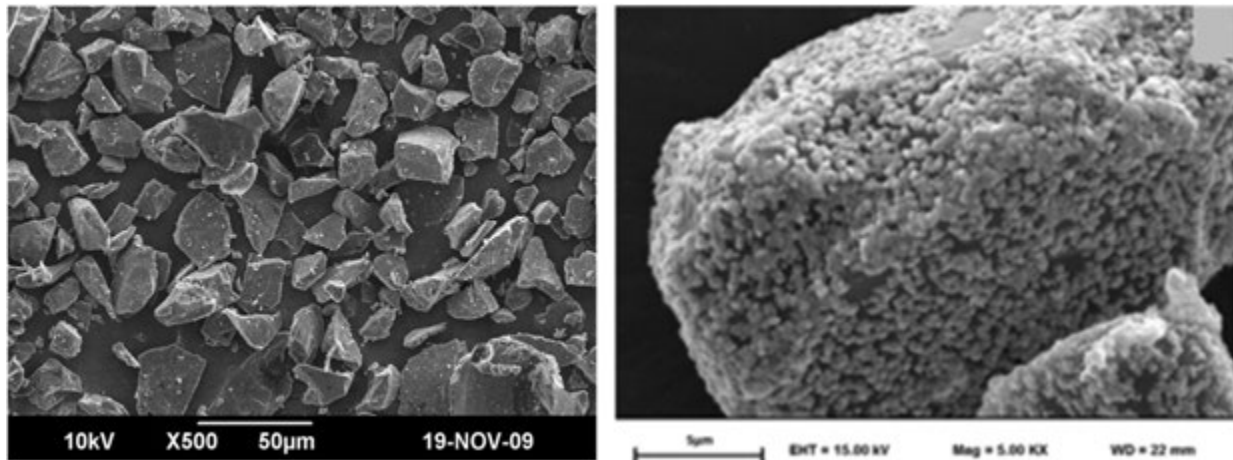


Fig. 9 SEM micrographs B₄C particles. Reproduced from Mahesh, V., Nair, P.S., Rajan, T., Pai, B., Hubli, R., 2011. Processing of surface-treated boron carbide-reinforced aluminum matrix composites by liquid–metal stir-casting technique. Journal of composite materials 45, 2371–2378.

mechanical properties. The in-situ composites show clean interfaces, strong interfacial bonding, a uniform spatial distribution of particles and a narrow particle size distribution. Further structural changes are effected using secondary processes such as mechanical working, infiltration, and controlled solidification ([Kampe et al., 1990](#); [Asthana, 1998b](#)).

Fig. 11(a) shows the microstructure of A390–0.5% Mg centrifugal cast In-situ functionally graded Al composite pistons fabricated by vertical centrifugal casting technique. Higher concentration of primary Si particles gets gradually distributed towards the head region of the piston providing enhanced properties. Magnesium provides substantial strengthening and improvement of precipitation hardening phases of aluminum alloy. Centrifugally cast FGM pistons provide high hardness, thermal resistance and wear properties than that of conventionally gravity cast pistons. Heat treated samples were found to provide superior properties than that of as-cast samples. A higher hardness of 188 BHN was reported in the head portion of the 0.5% Mg A390 FGM piston. Wear test results shows that the outer periphery of the piston is having lower wear rate even at high load (4 kg). Wear resistance gradually decreases from head to skirt portion. These Al FGM pistons containing a large quantity of primary Si particles on the piston head can meet the high temperature requirement and wear resistance of the piston ([Arsha et al., 2015](#)).

Hardness tests were performed on in situ alumina particle reinforced aluminum matrix composite through stir casting. Samples of Al–Al₂O₃ in situ composite, annealed samples of Al– Al₂O₃ in situ composite. Heat treated composite increases the workability and results in the formation of very fine precipitates and increases the strength and hardness. The compression strength of the Al–

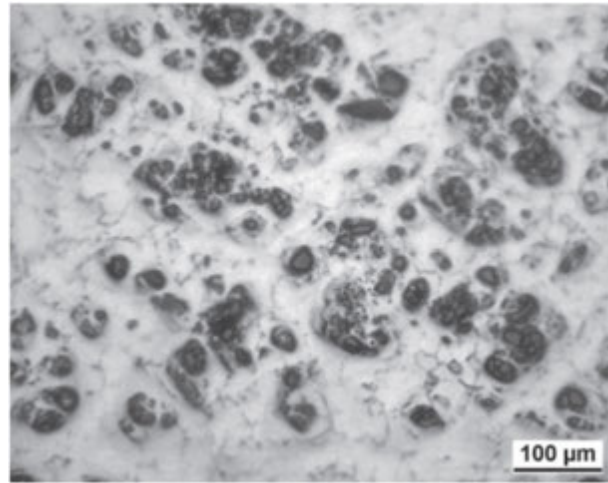


Fig. 10 Optical Micrograph of Al 6061-B₄C particles. Reproduced from Mahesh, V., Nair, P.S., Rajan, T., Pai, B., Hubli, R., 2011. Processing of surface-treated boron carbide-reinforced aluminum matrix composites by liquid-metal stir-casting technique. *Journal of composite materials* 45, 2371–2378.

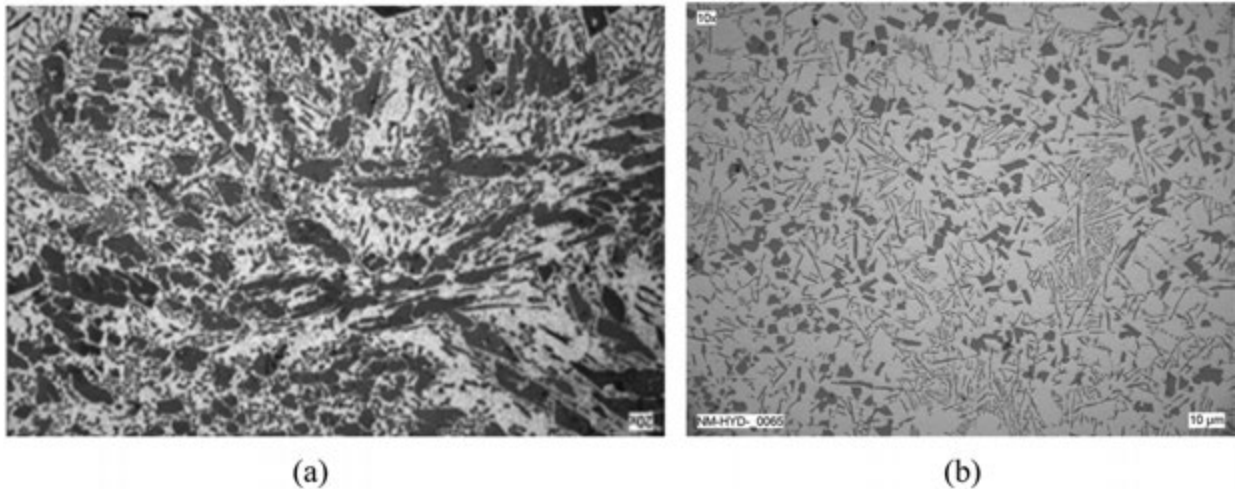


Fig. 11 (a) Microstructure of in-situ silicon reinforced Al composite, (b) Optical microstructure of Al-20 Ni in situ composite in as cast condition.

Table 7 Physical and mechanical properties of aluminum nickel composites

Material	Density (g/cm^3)	Hardness (Hv)	Impact strength (KJ/m^2)
Al 7075	2.905	165	21
Al 7075–0.5 Ni	2.917	177	34
Al 7075–1 Ni	2.927	186	53
Al 7075–1.5 Ni	2.951	193	74
Al 7075–2 Ni	2.962	198	93

Note: Kumar, A., Patnaik, A., Bhat, I., 2017. Investigation of nickel metal powder on tribological and mechanical properties of Al-7075 alloy composites for gear materials. *Powder Metallurgy* 60, 371–383.

Al₂O₃ in situ composite in annealed condition is 135 MPa and after solution treatment followed by ECAP pass and ageing increased it to 425 MPa.

Table 7 shows the physical and mechanical properties of aluminum nickel composites. From the table it is found that all the properties increases with increase in Nickel content. **Fig. 11(b)** shows the microstructure of Al-20 Ni in situ composite after heat treatment. Fine micron sized particles are uniformly distributed in the aluminum matrix and columnar crystal when Al₃Ni₂ is surrounded ([Rana et al., 2012](#)).

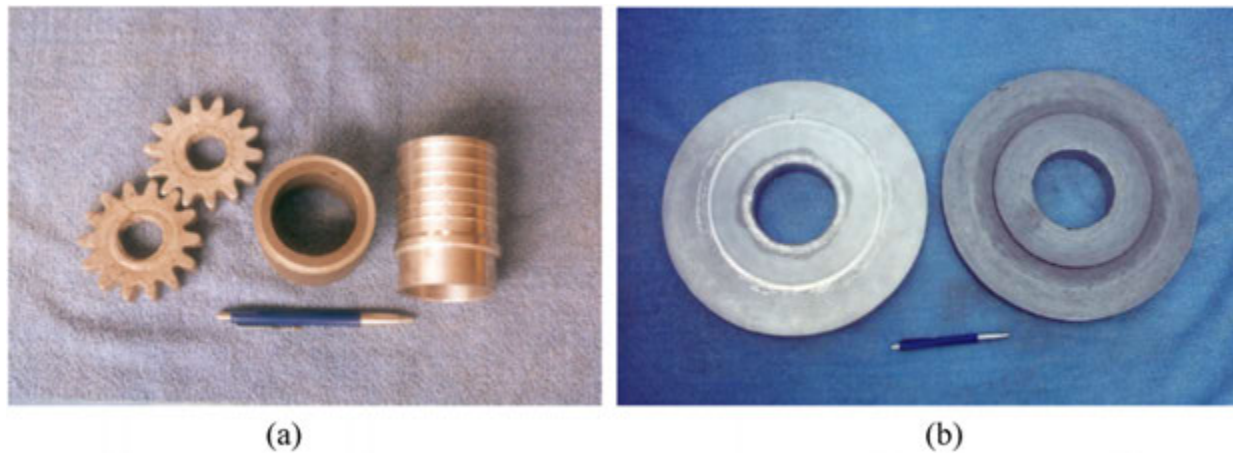


Fig. 12 Functionally graded aluminum matrix composite prototype components developed and fabricated by centrifugal casting for engineering applications. (a) Gear wheels and cylinder liner for two wheelers and (b) Brake rotor disc for four wheeler automobiles.

Table 8 Properties of reinforcements used in commercial aluminum matrix composites

System and manufacturer	Manufacturing process	Density (g/cm ³)	UTS (MPa)	Yield strength (MPa)	Modulus (GPa)	CTE ($\times 10^6$ K ⁻¹) (30–100°C)
A 360 10% SiC (Alcan)	Stir casting	2.65	310	221	91	21.4
A 380 10% SiC (Alcan)	Stir casting	2.76	345	241	93.8	19.3
A 6061 20% Al ₂ O ₃ (Alcan)	Stir casting	2.86	370	350	97.7	19.8
AA 2009 15.5% SiC (DWA Aluminum Composites)	Powder metallurgy	2.82	550	370	96	–
AA 6092 17.5% SiC (DWA)	Powder metallurgy	2.79	514	451	106	–
AA 6092 25% SiC (DWA)	Powder metallurgy	2.82	520	420	115	15.3
A 356.267% SiC ceramic processing Systems (CPS)	Infiltration	2.99	–	–	217	6.88
A 356.263% SiC (CPS)	Infiltration	3.01	–	–	192	7.96
A 356.254% SiC (CPS)	Infiltration	2.96	–	–	167	9.75

Note: Evans, A., San Marchi, C., Mortensen, A., 2003. Metal matrix composites. In: Metal Matrix Composites in Industry. Springer, pp. 9–38.

Applications

The properties of MMCs can differ by varying the nature of the constituent phases and their volume fractions. MMCs provide great potential for the production of composites with the desired properties for specific applications. Fig. 12 shows the functionally graded aluminum matrix composite prototype components developed and fabricated by centrifugal casting for engineering applications such as Gear wheels, cylinder liner for two wheeler and Brake rotor disc for four wheeler automobiles. Al based metal matrix composites (MMCs) are a class of materials that have proven effective in meeting most of the stringent requirements in applications where the necessary properties are lightweight, high rigidity and moderate strength. An area where substantial weight savings can be achieved by using MMCs is the components of the automotive braking system, such as the disc brakes and calipers. Table 8 describe the properties of reinforcements used in commercial aluminum matrix composites.

SiC reinforced aluminum brake rotors have been used for most modern car models, including Lotus Elise, General Motors EV1, Chrysler Prowler, Volkswagen Lupo 3 L and Toyota RAV4 EV. The Apollo spacecraft, the Skylab, the space shuttles and the International Space Station used AlMMCs and alloys. In such areas requiring mechanical stability, damping, thermal control and reduced weight, aluminum composites consistently surpass other metals. A variety of influential vehicle producers have adopted SiC-reinforced aluminum brake rotors for the widespread use of aluminum composite brake rotors due to the high cost and machinability problems of cast iron. To resolve price and machinability barriers, UWM developed aluminum-silicon carbide-graphite composites, aluminum alumina-graphite and hypereutectic aluminum-silicon graphite alloys with decreased silicon carbide (Nturanabo et al., 2019). Another application of MMCs in the automotive area is in diesel piston crowns. This involves incorporation of short fibers of alumina or alumina and silica in the crown of the piston. The conventional diesel engine piston has an Al–Si casting alloy with crown made of a nickel cast iron. The replacement of the nickel cast iron by aluminum matrix composite resulted in a lighter, more abrasion-resistant, and cheaper product. Continuous alumina fiber

reinforced Al composites are used to make power transmission cables. The cable consists of a composite core, consisting of $\text{Al}_2\text{O}_3/\text{Al}$ composite wrapped with Al–Zr wires. The composite core bears most of the load as it has much higher stiffness and strength (Rohatgi *et al.*, 2020).

Conclusion

This article has primarily been concerned with the factors influencing relationship of composites with micron sized reinforcements and the microstructural-mechanical properties. The effects of microstructure, particle distribution, volume fraction of reinforcement and the matrix have been reviewed. The physical and mechanical properties of micron sized reinforcements were also discussed with particular emphasis on strengthening mechanisms. The interface formed between the matrix and the reinforcement has a critical effect on subsequent mechanical behavior of the composite. Substantial progress in the development of light metal matrix composites has been achieved in recent decades, so that they could be introduced into the most important applications. This group of material becomes interesting for constructional and functional applications, if the properties of conventional materials either does not reach the increased standards of specific demands, or is the solution of the problem. The technology of MMCs is in competition with other modern material technologies. The advantages of the composite materials are realized when there is a reasonable cost performance relationship in the component production. The use of a composite material is essential if a special property profile can only be achieved by application of these materials.

Acknowledgment

The authors would like to thank the Director and Members of CSIR-NIIST for the support and encouragement, DST and IGSTC (NearNetMAC) for the funding.

References

- Arsha, A., Jayakumar, E., Rajan, T., Antony, V., Pai, B., 2015. Design and fabrication of functionally graded in-situ aluminium composites for automotive pistons. *Materials & Design* 88, 1201–1209.
- Asthana, R., 1998a. Reinforced cast metals: Part II Evolution of the interface. *Journal of Materials Science* 33, 1959–1980.
- Asthana, R., 1998b. Reinforced cast metals: Part I solidification microstructure. *Journal of Materials Science* 33, 1679–1698.
- Basak, A., Pramanik, A., Prakash, C., 2019. Deformation and strengthening of SiC reinforced Al-MMCs during in-situ micro-pillar compression. *Materials Science and Engineering: A* 763, 138141.
- Bhoi, N.K., Singh, H., Pratap, S., 2020. Developments in the aluminum metal matrix composites reinforced by micro/nano particles—a review. *Journal of Composite Materials* 54, 813–833.
- Bienia, J., Walczak, M., Surowska, B., Sobczaka, J., 2003. Microstructure and corrosion behaviour of aluminum fly ash composites. *Journal of Optoelectronics and Advanced Materials* 5, 493–502.
- Chawla, K.K., 2012. Metal matrix composites. In *Composite Materials Science and Engineering*. Springer. pp. 197–248.
- Clyne, T., Withers, P., 1995. *An Introduction to Metal Matrix Composites*. Cambridge University Press.
- Gül, H., Kılıç, F., Uysal, M., *et al.*, 2012. Effect of particle concentration on the structure and tribological properties of submicron particle SiC reinforced Ni metal matrix composite (MMC) coatings produced by electrodeposition. *Applied Surface Science* 258, 4260–4267.
- Jawalkar, C., Verma, A.S., Suri, N., 2017. Fabrication of aluminium metal matrix composites with particulate reinforcement: A review. *Materials Today: Proceedings* 4, 2927–2936.
- Kampe, S., Swope, G., Christodoulou, L., 1990. Axial alignment of short-fiber titanium aluminide composites by directional solidification. *MRS Online Proceedings Library Archive* 194.
- Karvanis, K., Fasnakis, D., Maropoulos, A., Papanikolaou, S., 2016. Production and mechanical properties of Al-SiC metal matrix composites. *IOP Conference Series: Materials Science and Engineering* 161, 012070.
- Knowles, A., Jiang, X., Galano, M., Audebert, F., 2014. Microstructure and mechanical properties of 6061 Al alloy based composites with SiC nanoparticles. *Journal of Alloys and Compounds* 615, S401–S405.
- Kumar, G.V., Rao, C., Selvaraj, N., Bhagyashekar, M., 2010. Studies on Al6061-SiC and Al7075-Al2O3 metal matrix composites. *Journal of Minerals & Materials Characterization & Engineering* 9, 43–55.
- Ling, Y., Wang, K., Li, W., Shi, G., Lu, P., 2019. Effect of slag on the mechanical properties and bond strength of fly ash-based engineered geopolymer composites. *Composites Part B: Engineering* 164, 747–757.
- Mahesh, V., Nair, P.S., Rajan, T., Pai, B., Hubli, R., 2011. Processing of surface-treated boron carbide-reinforced aluminum matrix composites by liquid–metal stir-casting technique. *Journal of Composite Materials* 45, 2371–2378.
- Manu, K.S., Rajan, T., Pai, B., 2016. Structure and properties of squeeze infiltrated zirconia grade-aluminosilicate short fiber reinforced aluminum composites. *Journal of Alloys and Compounds* 688, 489–499.
- Miracle, D., 2005. Metal matrix composites—from science to technological significance. *Composites Science and Technology* 65, 2526–2540.
- Nturanabo, F., Masu, L., Kirabira, J.B., 2019. Novel applications of aluminium metal matrix composites. In *Aluminium Alloys and Composites*. IntechOpen.
- Ozden, S., Ekici, R., Nair, F., 2007. Investigation of impact behaviour of aluminium based SiC particle reinforced metal–matrix composites. *Composites Part A: Applied Science and Manufacturing* 38, 484–494.
- Paknia, A., Pramanik, A., Dixit, A., Chattopadhyaya, S., 2016. Effect of size, content and shape of reinforcements on the behavior of metal matrix composites (MMCs) under tension. *Journal of Materials Engineering and Performance* 25, 4444–4459.
- Rajan, T., Pillai, R., Pai, B., 1998. Reinforcement coatings and interfaces in aluminium metal matrix composites. *Journal of Materials Science* 33, 3491–3503.
- Rana, R., Purohit, R., Das, S., 2012. Reviews on the influences of alloying elements on the microstructure and mechanical properties of aluminum alloys and aluminum alloy composites. *International Journal of Scientific and Research Publications* 2, 1–7.
- Rohatgi, P., Ray, S., Asthana, R., Narendranath, C., 1993. Interfaces in cast metal-matrix composites. *Materials Science and Engineering: A* 162, 163–174.

- Rohatgi, P.K., Kumar, P.A., Chelliah, N.M., Rajan, T., 2020. Solidification processing of cast metal matrix composites over the last 50 years and opportunities for the future. *JOM* 72.
- Sahin, Y., 2003. Preparation and some properties of SiC particle reinforced aluminium alloy composites. *Materials & Design* 24, 671–679.
- Surappa, M., 2008. Synthesis of fly ash particle reinforced A356 Al composites and their characterization. *Materials Science and Engineering: A* 480, 117–124.
- Taya, M., 1991. Strengthening mechanisms of metal matrix composites. *Materials Transactions, JIM* 32, 1–19.
- Wu, Y., Lavernia, E., 1992. Strengthening behavior of particulate reinforced MMCs. *Scripta Metallurgica et Materialia* 27, 173–178.
- Yan, C., Lifeng, W., Jianyue, R., 2008. Multi-functional SiC/Al composites for aerospace applications. *Chinese Journal of Aeronautics* 21, 578–584.

An Insight Into Metal Matrix Composites With Nano Size Reinforcement

Massoud Malaki, Isfahan University of Technology, Isfahan, Iran

© 2021 Elsevier Inc. All rights reserved.

An Overview

Composites are a pivotal category of advanced materials providing unique capability to improve selected properties. The improvement in targeted properties can be controlled, for example, through size, shape, and the amount of reinforcing agent. The research in composites primarily started in 1970s where the researchers tried to unify the metallic materials (as matrix) with ceramics (as reinforcement) where both continuous and discontinuous micro-sized strengthening materials were utilized through a number of manufacturing routes such as stir casting, powder metallurgy, rheocasting, etc. (Ceschini *et al.*, 2017a; Lloyd, 1994; Gupta and Wong, 2015).

Although conventional composites (i.e., those filled with the micron-sized reinforcements) may provide many benefits with respect to their neat alloys; however, owing to the micron size of the additive materials, these composites have a series of significant drawbacks such as excessive tool wear rate while machining, poor ductility, and low fracture toughness as compared to the unfilled matrices (Malaki *et al.*, 2019; Suresh, 2013). To deal with the mentioned limitations and to fabricate novel composites with simultaneously improved strength and ductility at both room and elevated temperatures, the size of strengthening agent has been reduced to the nanosized levels (< 100 nm) in order to provide metal matrix nanocomposites (MMNCs). Since 2000, the interest in using nano-sized reinforcing agent in metals such as Al, Mg, Ti, Ni, and Cu sharply increased. The reinforcements were first from oxides, carbides, nitrides or borides, but carbon allotropes such as buckyballs, CNTs, MWCNTs, graphene, and other carbon based nanoplatelets were then considered in the investigations (Calvert, 1999; Suárez *et al.*, 2016; Malaki *et al.*, 2019; Ceschini *et al.*, 2017a). Using nanosized reinforcements, the properties mentioned below can be improved:

- (1) Mechanical strengths at room or elevated temperatures,
- (2) Fatigue,
- (3) Fracture toughness,
- (4) Creep,
- (5) Wear and corrosion,
- (6) Thermal properties,
- (7) Damping,
- (8) Machinability.

The two prevalently reported damage mechanisms in the micro-sized metal matrix composites are particle breakage and reinforcement-matrix interfacial debonding; these two mechanisms are substantially minimized in the nano-composites (Suresh, 2013). Using nano-sized strengthening reinforcements, ductility and fracture toughness behaviors improve, being highly demanded in special applications such as biomaterials (Hassan and Lewandowski, 2018; Ceschini *et al.*, 2017a; Goh *et al.*, 2008; Zhong *et al.*, 2007; Gupta and Wong, 2015; Ceschini *et al.*, 2017b; Goh *et al.*, 2006).

Regardless of reinforcement and matrix properties, manufacturing and processing conditions are of crucial importance as the final properties are directly influenced by the homogeneity and the dispersion quality of the reinforcing agent (Ceschini *et al.*, 2017b; Malaki *et al.*, 2019). Furthermore, most of the reinforcing particles such as ceramic particles have poor wetting conditions, so a careful consideration should be made in order to achieve good interfacial bonding between matrix and reinforcement surfaces. For instance, during stir casting, ultrasonic dispersion of ceramic or carbide nanoparticles in molten matrix, e.g., Al, is a method of improving wettability (Malaki *et al.*, 2019; Abdullah *et al.*, 2012; Eskin and Eskin, 2015).

Metal matrix nanocomposites dedicated with excellent combinations of material and mechanical properties are inaugurating new applications in different engineering and biomedical fields (Gupta and Meenashisundaram, 2015). For instance, nano-bio-composites provide enhanced specific strength, acceptable biocompatibility, and biodegradation behaviors as well as cell growth capability typically demanded in biomaterials like orthopedic implants (Gong *et al.*, 2015; Gupta and Meenashisundaram, 2015; Paul and Sharma, 2006). In addition, light-weight and high-strength are simultaneously needed in many industrial applications, like those used in motorbikes in order to save cost, reduce weight, and improve performance (Eskin and Eskin, 2014; Gupta and Wong, 2015).

Strengthening Mechanisms

Reinforcements may change dislocation density, structure, and movement and hence may considerably influence the mechanical performance of the fabricated composites (Hamedan and Shahmiri, 2012; Ceschini *et al.*, 2017a; Shin and Bae, 2018; Malaki *et al.*, 2019). Although the nature of the MMNCs has not yet been fully understood, many efforts have been made to find out the role played by the strengthening mechanism(s) and propose constitutive modeling techniques (Baisane *et al.*, 2015; Ceschini *et al.*, 2017b; Habibnejad-Korayem *et al.*, 2009; Zhang and Chen, 2008; Kim *et al.*, 2013; Sanaty-Zadeh, 2012). Here are some of the most important strengthening mechanisms.

Orowan

Unlike those traditional composites reinforced by coarse micron-sized particles having relatively large interparticle distances, nanocomposites are with very closely spaced nano-particles posing an effective strengthening mechanism, i.e., Orowan (Ceschini *et al.*, 2017b; Habibnejad-Korayem *et al.*, 2009; Zhang and Chen, 2008; Zhang and Chen, 2006). The effect of Orowan strengthening is more pronounced in case very fine particles are homogeneously well-dispersed and well-distributed throughout the bulk of composite (Malaki *et al.*, 2019; Zhang and Chen, 2008; Zhang and Chen, 2006). As the dislocations reach to a reinforcing hard particle, e.g., a ceramic nanoparticulate, they first bend and reconnect with themselves on the other side creating a kind of dislocation loop around the reinforcement particles (Ceschini *et al.*, 2017a,c). The dislocation itself can then continue to propagate through the host matrix. While Eq. (1) presents the contribution of Orowan strengthening to the strength (Lloyd, 1994), the interparticle space, λ , is given by Eq. (2) wherein d_p is the average diameter of the nanoparticles, b the Burgers vector, G_m the shear modulus, and V_p the vol% fraction of reinforcing agent (Malaki *et al.*, 2019):

$$\Delta\sigma_{OR} = \frac{0.13bG_m}{\lambda} \ln \frac{d_p}{2b} \quad (1)$$

$$\lambda = d_p \left[\left(\frac{1}{2V_p} \right)^{1/3} - 1 \right] \quad (2)$$

It was shown that the contribution of Orowan strengthening is substantially diminished when the nanoparticles are aggregated in clusters. Below 100 nm particle size, the contribution is particularly effective and increases as the particle size decreases up to a critical value (Malaki *et al.*, 2019). The critical size for the Al_2O_3 -reinforced magnesium matrix nanocomposite and Y_2O_3 -reinforced titanium matrix composites is ~ 5.44 times Burger vector (Ceschini *et al.*, 2017a,b).

Hall-Petch

The addition of nano particles leads to a microstructural grain refinement and hence an increased yield strength is expected. This increase in yield strength can be presented by Eq. (3), called the Hall-Petch equation (Hall, 1951; Petch, 1953) and Eq. (4) (Kim *et al.*, 2013) where σ_y is the yield strength, σ_0 the friction stress that allows dislocations to move on slip planes in a single crystal in the absence of any strengthening mechanisms, k_y the stress concentration factor, and D the average grain size. Also, D_{MMNC} and D_0 are the grain sizes of the nanocomposite and the unreinforced alloy:

$$\sigma_y = \sigma_0 + k_y D^{-1/2} \quad (3)$$

$$\Delta\sigma_{GR} = k_y \left(\frac{1}{\sqrt{D_{MMNC}}} - \frac{1}{\sqrt{D_0}} \right) \quad (4)$$

The contribution of grain refinement was found to be low in some cases (Goh *et al.*, 2007) or it was omitted by some others (Zhang and Chen, 2006, 2008); however, Habibnejad-Korayem *et al.* (2009) observed more than 15% contribution to the final strength of Al_2O_3 reinforced magnesium matrix nanocomposite. In 2013, Kim *et al.* (2013) reviewed the magnesium metal matrix nanocomposites where they concluded that grain refinement is a main factor influencing the total strength of many magnesium matrix composites.

Mismatch in the Coefficient of Thermal Expansion (CTE)

After nano-reinforcements are stirred in a composite slurry, stresses appear at the interface after it is left to cool down, usually due to significantly different coefficients of thermal expansion (CTEs) between the nanoparticles and the host metal. The mentioned difference in CTEs provides geometrically necessary dislocations (GNDs) by which the differences of the CTEs could be accommodated. The GNDs-induced mechanical strength can be described by Eq. (5) (Dai *et al.*, 2001a; Vogt *et al.*, 2009) wherein β is the dislocation strengthening coefficient, ΔT the difference in temperature, and $\Delta\alpha$ the difference in CTE:

$$\Delta\sigma_{CTE} = \sqrt{3} \beta G_m b \sqrt{\frac{12V_p \Delta\alpha \Delta T}{b d_p}} \quad (5)$$

It was shown that the contribution of very small reinforcing agent to the strength increase due to mismatch in the CTE is somewhat negligible (Dunand and Mortensen, 1991; Redsten *et al.*, 1995).

Mismatch in the Young's Modulus

Similar to the mismatch in CTEs, GNDs can also be generated due to differences in the Young's modulus (MYD). Dai *et al.* (2001a) proposed Eq. (6) to describe the contribution of MYD in mechanical strength improvement. α is material coefficient and ε is the bulk strain of the composite:

$$\Delta\sigma_{Mod} = \sqrt{3} \alpha G_m b \sqrt{\frac{6V_p \varepsilon}{b d_p}} \quad (6)$$

Load-Bearing

The shear transfer of applied load from the matrix to the reinforcing agent is named as load-bearing/transferring effect. This kind of strengthening mechanism can be dominant provided that a strong cohesion is obtained between the reinforcement and matrix (Malaki *et al.*, 2019). Since nanocomposites contain only a very low volume fraction of the reinforcements (<5%), the effect of load-bearing was found to be low (Goh *et al.*, 2007) or even negligible (Habibnejad-Korayem *et al.*, 2009) as shown in Eq. (7) (Ramakrishnan, 1996); σ_m is the yield strength of the matrix:

$$\Delta\sigma_{\text{Load}} = \frac{1}{2}V_p\sigma_m \quad (7)$$

Modeling

Since 1980s, many modeling approaches have been developed so far among which the following three models are frequently used in order to estimate the yield strength of MMNCs (Kim *et al.*, 2013):

- Arithmetic summation,
- Quadratic summation,
- Compounding methods.

The first two models, arithmetic and quadratic summations, are based on dislocation theory applied to single crystals (Ceschini *et al.*, 2017a,b). The third model, i.e., compounding method, was originally proposed by Nardone and Prewé (1986). Based on modified shear lag, the compounding methods treat all mechanisms as load-bearing effects being represented by a summation of strengthening factors. In order to calculate the effects of strengthening mechanisms, the rule of addition was firstly introduced by Arsenault (1984); this model overestimates the yield strength in some cases (Goh *et al.*, 2007). Ramakrishnan (1996) integrated a modified shear lag approach and an improved dislocation density method wherein the effects of load transfer and the coefficient of thermal expansion are taken into account. Zhang and Chen (2006) modified the Ramakrishnan's model in order to include Orowan strengthening effect in the calculation, being specifically significant in the case of MMNCs.

The effects that reinforcing nanoparticles have on mechanical strength typically include some different strengthening mechanisms taking action in varying levels whose contributions to the final strength improvement could be summed up by Eq. (8) or the root of the sum of the squares could be considered as a total effect (Eq. (9)) (Goh *et al.*, 2007; Zhong *et al.*, 2007). Eq. (8) is usually employed when the reinforcing effects are supposed to be independent, while Eq. (9) is commonly utilized when the individual mechanisms do not behave independently:

$$\Delta\sigma_{\text{Total}} = \Delta\sigma_{\text{GR}} + \Delta\sigma_{\text{OR}} + \Delta\sigma_{\text{CTE}} + \Delta\sigma_{\text{Mod}} + \Delta\sigma_{\text{Load}} \quad (8)$$

$$\Delta\sigma_{\text{Total}} = \sqrt{\Delta\sigma_{\text{GR}}^2 + \Delta\sigma_{\text{OR}}^2 + \Delta\sigma_{\text{CTE}}^2 + \Delta\sigma_{\text{Mod}}^2 + \Delta\sigma_{\text{Load}}^2} \quad (9)$$

Depending on materials, processing conditions, or manufacturing routes, some of these strengthening effects can be omitted from the calculations. For an instance, the effect of load transferring effect is insignificant when using a very low volume fraction of reinforcing particles; the effect of Orowan strengthening can be neglected when the particle size is not adequately small. Although many believe the model described in Eq. (9) is best fit with the experimental data (Goh *et al.*, 2007; Dai *et al.*, 2001a; Sanaty-Zadeh, 2012), still there is no general formula to calculate the strength of MMNCs (Kim *et al.*, 2013).

It should be noted that no agglomeration or clustering has yet been taken into consideration by the current models. Post-processing techniques such as mechanical deformation utilized in many studies usually increase dislocation density and hence the final yield strength improvement may be influenced as well by the work hardening caused by these post-processing methods.

Manufacturing and Processing Techniques

Fabrication of MMNCs is of crucial importance as the final performance is significantly affected by the manufacturing parameters (Malaki *et al.*, 2019; Ceschini *et al.*, 2017b; Suresh, 2013; Eskin and Eskin, 2015). Here are the most important fabrication methods for the MMCs.

Stir Casting

One of the most prevalent, simple, fast, and even economic methods of producing MMCs is stir-casting wherein the reinforcing agent is added to a metal melt followed by a stirring process to achieve a homogenously distributed particles in the metal matrix. Aluminum and magnesium alloys are the two metals extensively used as a matrix being reinforced by a wide variety of materials ranging from ceramics, oxides, and nitrides to carbon allotropes such as nanotubes and graphene (Hemanth, 2009; Hamedan and Shahmiri, 2012; Sajjadi *et al.*, 2011; Suresh *et al.*, 2011). Apart from several advantages, stir casting has a few major drawbacks from which poor wetting condition of nanoparticles in a metal melt, the tendency of particles to be clustered or agglomerated due to high interparticle van der Waals, and the porosities (e.g., voids and cavities) are of the most important items (Cao *et al.*, 2008;

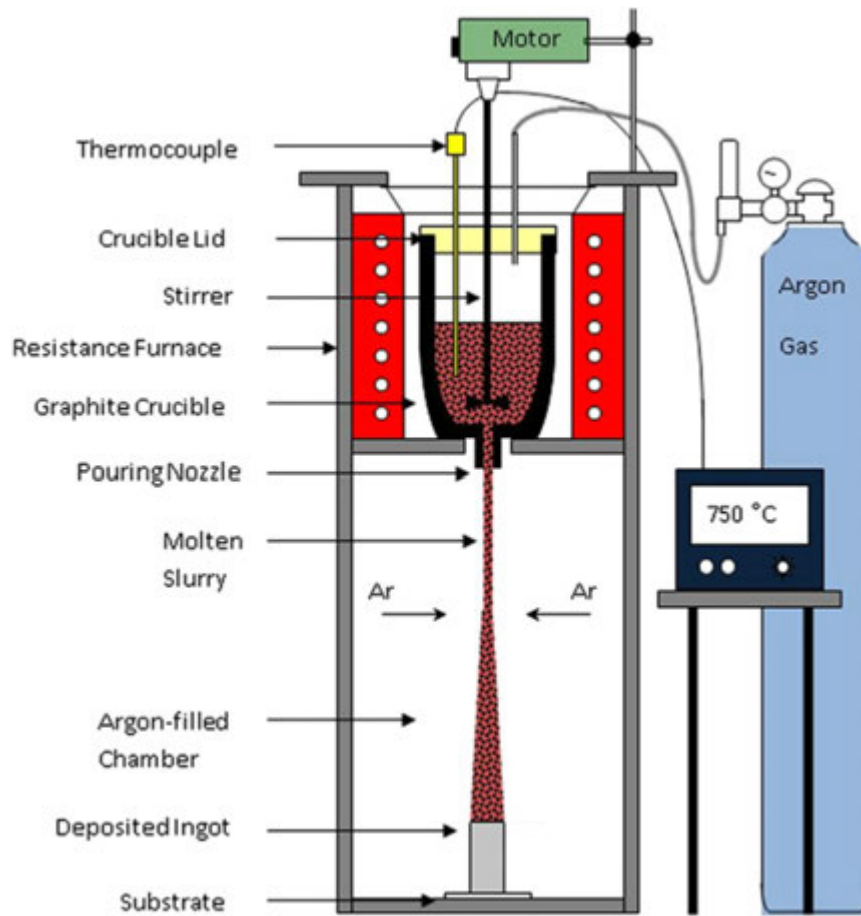


Fig. 1 Schematic diagram of disintegrated melt deposition setup. Reproduced from Gupta, M., Wong, W., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.

Donthamsetty *et al.*, 2009; Akbari *et al.*, 2013). Ultrasonic treatment is sometimes applied to improve wettability and dispersion quality (Malaki *et al.*, 2019). To minimize casting voids and porosity, cast materials are usually further processed by forging, extrusion, swaging, or other plastic deformation methods (Malaki *et al.*, 2019; Goh *et al.*, 2007; Rozak *et al.*, 1992; Goh *et al.*, 2008; Hassan and Lewandowski, 2018).

Disintegrated Melt Deposition (DMD)

Based on stir casting principles, the composite slurry is first prepared in a crucible and then passed through a nozzle onto a metallic substrate at a superheated temperature under the protection of an inert gas jet. Fig. 1 shows the schematic of DMD process. DMD is mainly used to produce magnesium matrix composites (Goh *et al.*, 2006; Srivatsan *et al.*, 2012; Ho *et al.*, 2004; Goh *et al.*, 2008, 2007). For example, Srivatsan *et al.* (2013) could fabricated AZ31 reinforced 1.5 vol% Al_2O_3 (50 nm size) using DMD wherein the ingots were post-extruded resulting in a final product with much finer microstructure and enhanced mechanical performance than that of un-reinforced AZ31.

Semi-Solid Casting (SSC)

Semi-solid casting is a die casting method, wherein a metal with liquid/solid state is injected into a mold. Casting in this condition requires lower power and the resultant product has less voids and porosities, hence demands less post-processings such as machining or mechanical plastic deformation in order to improve microstructure. On the other hand, globular microstructure is not easy to obtain in SSC. Zinc alloy AC43A nanocomposite with 0.5 wt% SiC β nanoparticle additions were cast at a 30% solid fraction (de Cicco *et al.*, 2009). AM60/SiC nanocomposite was obtained in a uniform microstructure form via semi-solid casting and a 19.3% and 7.9% increase in the elongation and the UTS, respectively, was discerned through addition of 0.1 vol% of the nanoparticles (Wang *et al.*, 2006).

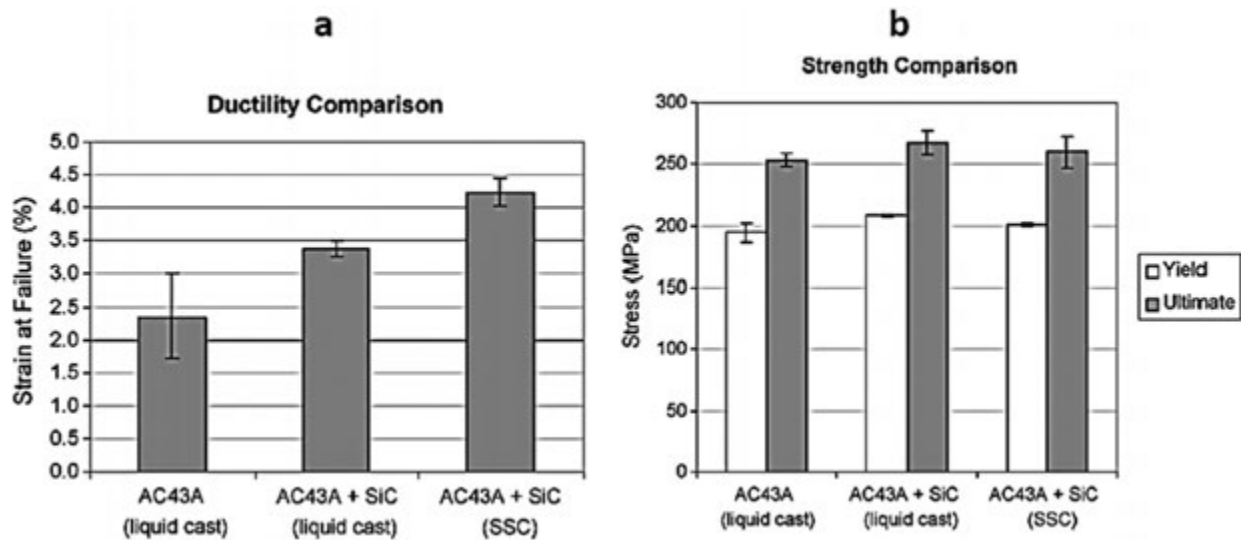


Fig. 2 Comparison of mechanical performance among liquid cast AC43A alloy, liquid cast AC43A/0.5 wt% SiC nanocomposite, and AC43A/0.5 wt% SiC nanocomposites produced by SSC at 30% solid fraction: (a) ductility and (b) strength. Reproduced from de Cicco, M.P., 2009. Solidification phenomena in metal matrix nanocomposites (PhD Thesis). University of Wisconsin.

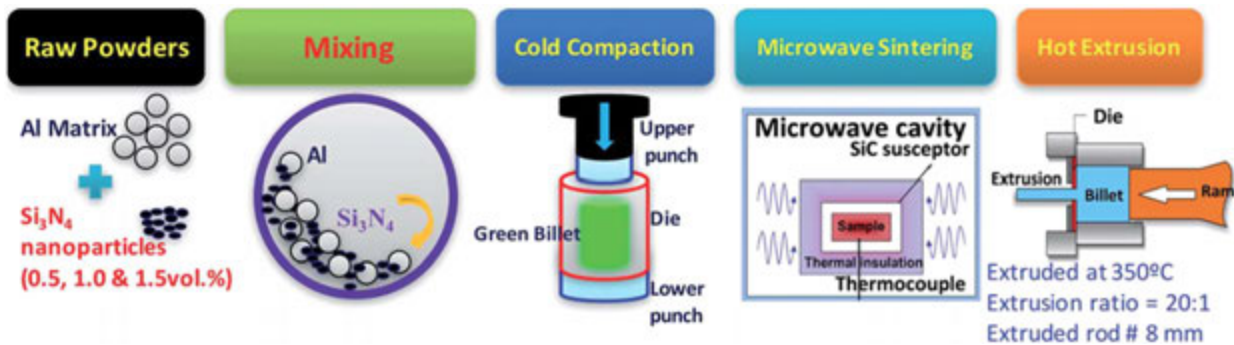


Fig. 3 Different steps toward the production of Al-Si₃N₄ nanocomposites. Reproduced from Matli, P.R., Ubaid, F., Shakoor, R.A., *et al.*, 2017. Improved properties of Al-Si₃N₄ nanocomposites fabricated through a microwave sintering and hot extrusion process. RSC Advances 7, 34401–34410.

de Cicco *et al.* (2009) and de Cicco (2009) dealt with the semi-solid casting of zinc alloy AC43A nanocomposite with 0.5 wt% SiC β reinforcement and a solid fraction of 30% wherein they observed reduced shrinkage, increased ductility & strength, and nanoparticle induced grain refinement producing a globular structure without having to apply additional material/mechanical processings. Fig. 2 illustrates the ductility as well as strength obtained under different conditions showing both strength and ductility improvement in case SSC is used to fabricate the composite.

Powder Metallurgy (PM)

Powder metallurgy consists three distinct steps, i.e., (1) mixing metal and reinforcement powders, (2) powder compaction to produce green materials, and (3) sintering usually followed by a deformation process such as hot extrusion (Matli *et al.*, 2017). As a solid-state process, powder metallurgy has a lot of advantages including the following items:

- (1) Near-net shape parts are commonly produced by PM.
- (2) A considerable weight fractions of the nanoparticles can also be integrated.
- (3) PM can be used in batch production systems such as automotive industries.

A wide variety of materials have been used as matrix or reinforcing agent in order to produce different nanocomposites based on PM; for instance, Matli *et al.* (2017) employed a novel MW sintering followed by extrusion at elevated temperatures to develop a Si₃N₄ reinforced nanocomposite with different vol% of 0.5%, 1.0%, and 1.5% (Fig. 3); Simões *et al.* (2017) fabricated CNTs reinforced aluminum and nickel matrix composites with 0.5–2.0 wt%; van Pham *et al.* (2011) produced a CNT reinforced

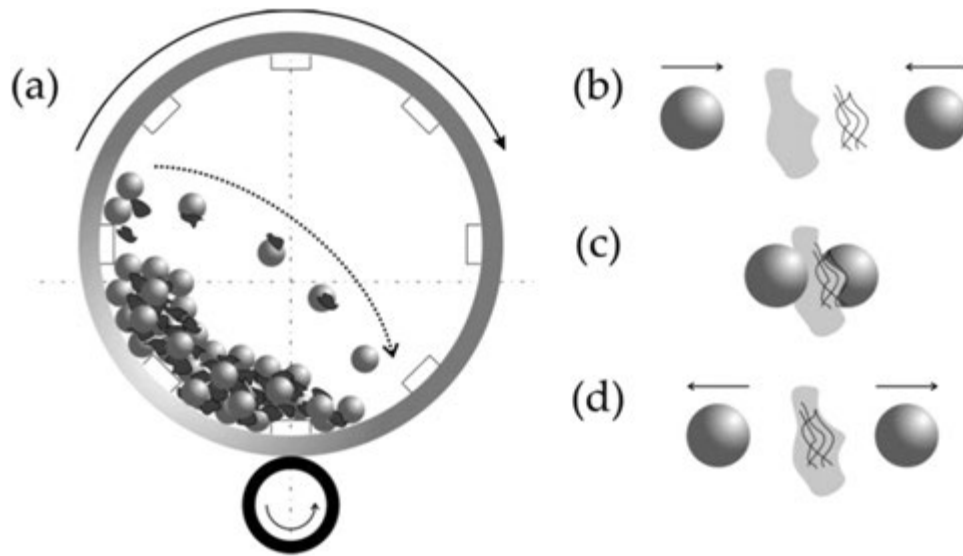


Fig. 4 Schematic of the ball milling process (a). The used balls are hitting the reinforcements and the matrix powder material (b), welding and integrating the two components (c) and bounce of the powder particle to restart this process again at another spot (d). Reproduced from Suárez, S., Reinert, L., Mücklich, F., 2016. Carbon nanotube (CNT)-reinforced metal matrix bulk composites: Manufacturing and evaluation. *Diamond and Carbon Composites and Nanocomposites*. InTech.

nanocomposite having 0–3.5 wt% CNTs; Akbarpour *et al.* (2014) developed SiC nanoparticles reinforced copper. All these papers reported that the addition of nano reinforcing agents could improve mechanical performance.

A branch of powder metallurgy involves mechanical mixing during which a high energy ball milling process is utilized wherein the cold welding, fracture, and re-welding of the particles occur (Suryanarayana and Al-Aqeeli, 2013; Suryanarayana, 2011, 2001). In particular, this practice is favorable while producing those composites reinforced by nano-sized ceramic particles for breaking up the agglomerates and homogeneously distributing reinforcements throughout the base matrix (Ye *et al.*, 2006). Rotational speed, time of milling as well as the ratio of ball-to-powder are of the most important parameters during ball milling (Fig. 4).

Friction Stir Processing (FSP)

Evolved from the basic principles of friction stir welding (FSW), FSP has now been widely utilized in different researches and industrial sectors where a locally intense severe plastic deformation is applied on the material leading to improved microstructural features and mechanical properties (Arora *et al.*, 2012). The required deformation is commonly provided by a non-consumable cylindrical pin being forcibly inserting into a groove filled with the pre-determined weight fraction of the nanoparticles (Morisada *et al.*, 2006; Lee *et al.*, 2006; Shafiei-Zarghani *et al.*, 2009; Yang *et al.*, 2010; Sharifitabar *et al.*, 2011; Asadi *et al.*, 2011; Mazaheri *et al.*, 2011; Hsu *et al.*, 2006, 2005; Zhang *et al.*, 2011; Bauri *et al.*, 2011); the pin rotates in a stirring movement, heats up the processing region, and disperses the particles within the adjacent base metal (Fig. 5). This process has mostly been used in the fabrication of light-weight metal matrix (e.g., aluminum and magnesium) nanocomposites (Alizadeh *et al.*, 2013). It should be noted that the uniform distribution of nano-reinforcing agent and final surface quality are the two challenges with the FSP (Bauri *et al.*, 2011; Zhang *et al.*, 2011).

Morisada *et al.* (2006) investigated the optimum tool speed of FSPed multi-walled CNTs reinforced magnesium matrix (AZ31) nanocomposites; it was shown that the synergistic effects of FSP and the addition of nano MWCNTs could improve the mechanical strength and refine the microstructure significantly at the pin rotation of 1500 rpm and traverse motion of 25 mm/min.

Lim *et al.* (2009) employed FSP to fabricate multi-walled CNT reinforced aluminum alloy where they found that increasing the pin speed from 1500 and 2500 rpm and the pin penetration depth promotes the dispersion quality of the reinforcing particles; however, fully homogeneity could not be obtained when the MWCNTs are fractured and or tangled during the processing. It is believed that increasing FSP passes could further improve the dispersion and the homogeneity of the particles within the metal matrix (Lee *et al.*, 2006).

Accumulative Roll Bonding (ARB)

ARB is a process by which metal matrix nanocomposites can also be produced. ARB is a severe plastic deformation (SPD) process wherein a stack of sheets are rolled, sectioned, piled a few times to produce final layered materials (Saito *et al.*, 1998; Ghalehbandi *et al.*, 2019). To further improve the ARBed materials, nano-reinforcing particles are embedded between the layers (Alizadeh *et al.*, 2013; Darmiani *et al.*, 2013). As shown in Fig. 6, the process involves the following steps: (1) surface treatment and wire brushing

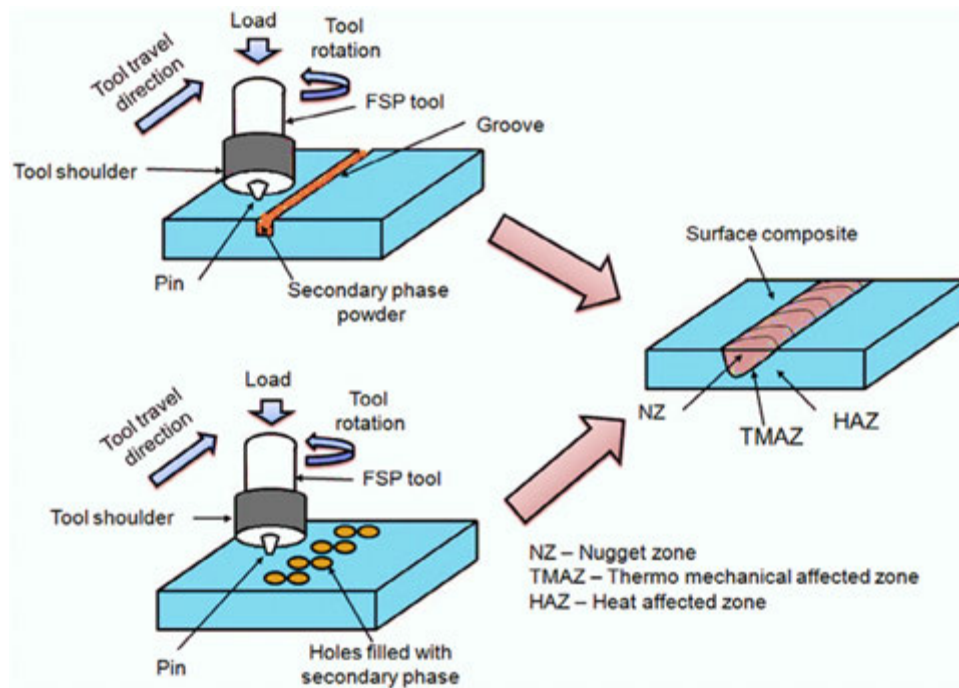


Fig. 5 Fabrication of metal matrix nanocomposite by friction stir processing (FSP). Reproduced from Sunil, B.R., Reddy, G.P.K., Patle, H., Dumpala, R., 2016. Magnesium based surface metal matrix composites by friction stir processing. *Journal of Magnesium and Alloys* 4, 52–61.

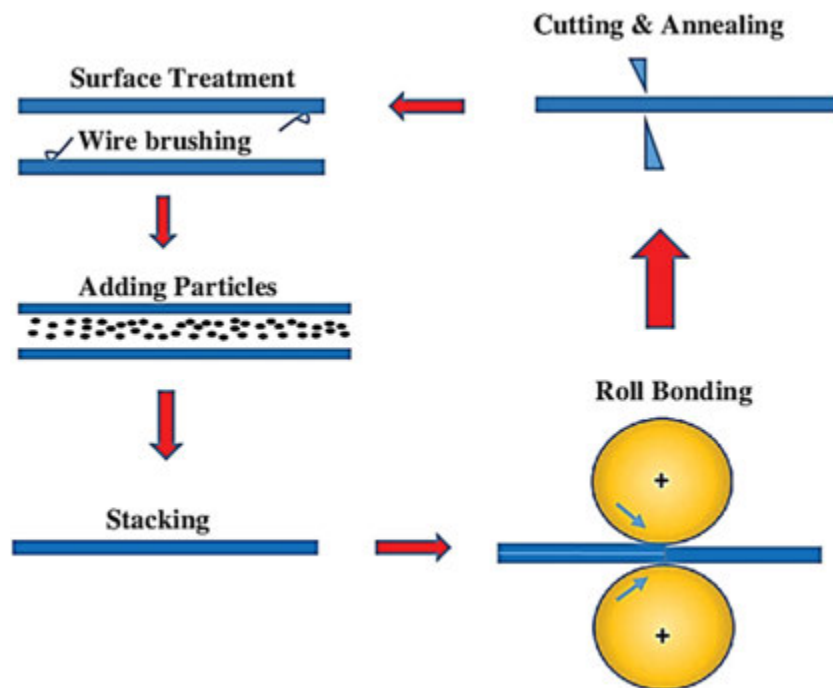


Fig. 6 Schematic representation of accumulative roll bonding (ARB) for the fabrication of metal matrix nanocomposites.

in order to remove contaminants and unwanted layers of oxides and so on, (2) adding reinforcing particles between the sheets, (3) stacking, (4) rolling the sheets up to a significant thickness reduction, and finally (5) cutting the ARBed specimen and annealing (if needed); the process can be repeated many times (Darmiani *et al.*, 2013; Ceschini *et al.*, 2017a,b).

To date different kinds of reinforcing agents, e.g., W (Amirkhanlou *et al.*, 2013; Liu *et al.*, 2013), WC (Liu *et al.*, 2012), SiO₂ (Hashemi *et al.*, 2012), CNT (Karimi *et al.*, 2016), SiC (Amirkhanlou *et al.*, 2011; Jamaati *et al.*, 2011; Alizadeh and Paydar, 2010),

TiO₂ (Soltani *et al.*, 2012), Al₂O₃ (Jamaati and Toroghinejad, 2010), and B₄C (Yazdani and Salahinejad, 2011) have been used in the reinforced ARBed aluminum composites. For ARB has successfully been utilized to fabricate magnesium matrix nano-composite (for instance, CNT reinforced Mg) (Lv *et al.*, 2017) as well those composites with different material matrices (for example, Al–Al₂O₃–Mg) (Abbasi and Sajjadi, 2018).

Homogenous dispersion and the number of ARB passes seem to have a significant effect on the output mechanical performance (Jamaati *et al.*, 2012). Work hardening, grain refinement, and more uniform distribution of reinforcing particles are the main factors affecting the final ARB products (Ceschini *et al.*, 2017a,b; Jamaati *et al.*, 2011; Jamaati and Toroghinejad, 2010). For instance, the mechanical property of WO₃ (1.0, 1.5, and 2 vol. fractions) reinforced aluminum nanocomposites significantly enhanced upon 12 ARB passes (Khabushan and Bonabi, 2017).

Summary and Conclusion

Light-weight high-strength metal matrix nano-composites (MMNCs) can be used in a wide variety of applications, e.g., aerospace, automotive, and biomedical engineering, owing to their sustainability, increased specific strength/stiffness, enhanced elevated temperature strength, improved wear or corrosion resistance. Metal matrix nanocomposites are commonly those light-weight metals like aluminum or magnesium that are usually reinforced by ceramic particulates, carbon allotropes, elementals, oxides, nitrides, etc. Due to nano-sized dimensions, nanoparticles have a very high aspect ratio, make them to easily agglomerate due to interparticle interactions such as van der Waals. Using well-dispersed fine particles within the host matrix leads to improve strength and ductility simultaneously which is too hard to obtain in micro-composites. It is repeatedly reported that those composites reinforced by smaller particle size exhibit far better mechanical properties such as improved fatigue strength (Hassan and Lewandowski, 2018, 2014; Xia *et al.*, 2019; Ceschini *et al.*, 2017a,b; Malaki *et al.*, 2019). To fabricate the MMNCs, many manufacturing techniques have already been developed, e.g., solid-state processing techniques such as powder metallurgy, liquid state processing routes such as stir casting and semi-solid-state processing methods. To date, a wide variety of particles with different shapes, sizes, and properties have been utilized in MMNC production systems from which ceramic nanoparticles were frequently used, probably due to superior mechanical strength, excellent wear behavior, and thermal stability of ceramic particles. Particles with smaller size. Extensive research investigations are now being conducted to further develop the MMNCs and the technological issues, all trying to fabricate and commercialize high performance metal matrix nanocomposites.

References

- Abbasi, M., Sajjadi, S., 2018. Manufacturing of Al–Al₂O₃–Mg multilayered nanocomposites by accumulative roll bonding process and study of its microstructure, tensile, and bending properties. *Journal of Composite Materials* 52, 147–157.
- Abdullah, A., Malaki, M., Baghizadeh, E., 2012. On the impact of ultrasonic cavitation bubbles. *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science* 226, 681–694.
- Akbari, M.K., Mirzaee, O., Baharvandi, H., 2013. Fabrication and study on mechanical properties and fracture behavior of nanometric Al₂O₃ particle-reinforced A356 composites focusing on the parameters of vortex method. *Materials & Design* 46, 199–205.
- Akbarpour, M., Salahi, E., Hesari, F.A., Simchi, A., Kim, H., 2014. Microstructure and compressibility of SiC nanoparticles reinforced Cu nanocomposite powders processed by high energy mechanical milling. *Ceramics International* 40, 951–960.
- Alizadeh, M., Paydar, M., 2010. Fabrication of nanostructure Al/SiCp composite by accumulative roll-bonding (ARB) process. *Journal of Alloys and Compounds* 492, 231–235.
- Alizadeh, M., Beni, H.A., Ghaffari, M., Amini, R., 2013. Properties of high specific strength Al–4wt% Al₂O₃/B₄C nano-composite produced by accumulative roll bonding process. *Materials & Design* 50, 427–432.
- Amirkhanlou, S., Jamaati, R., Niroumand, B., Toroghinejad, M.R., 2011. Fabrication and characterization of Al/SiCp composites by CAR process. *Materials Science and Engineering: A* 528, 4462–4467.
- Amirkhanlou, S., Ketabchi, M., Parvin, N., Khorsand, S., Bahrami, R., 2013. Accumulative press bonding; a novel manufacturing process of nanostructured metal matrix composites. *Materials & Design* 51, 367–374.
- Arora, H., Singh, H., Dhindaw, B., 2012. Composite fabrication using friction stir processing – A review. *The International Journal of Advanced Manufacturing Technology* 61, 1043–1055.
- Arsenault, R.J., 1984. The strengthening of aluminum alloy 6061 by fiber and platelet silicon carbide. *Materials Science and Engineering* 64, 171–181.
- Asadi, P., Faraji, G., Masoumi, A., Givi, M.B., 2011. Experimental investigation of magnesium-base nanocomposite produced by friction stir processing: Effects of particle types and number of friction stir processing passes. *Metallurgical and Materials Transactions A* 42, 2820–2832.
- Baisane, V., Sable, Y., Dhobe, M., Sonawane, P., 2015. Recent development and challenges in processing of ceramics reinforced Al matrix composite through stir casting process: A review. *International Journal of Engineering and Applied Sciences* 2, 11–16.
- Bauri, R., Yadav, D., Suhas, G., 2011. Effect of friction stir processing (FSP) on microstructure and properties of Al–TiC in situ composite. *Materials Science and Engineering: A* 528, 4732–4739.
- Calvert, P., 1999. Nanotube composites: A recipe for strength. *Nature* 399, 210.
- Cao, G., Choi, H., Oportus, J., Konishi, H., Li, X., 2008. Study on tensile properties and microstructure of cast AZ91D/AlN nanocomposites. *Materials Science and Engineering: A* 494, 127–131.
- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2017b. Aluminum and magnesium metal matrix nanocomposites. Springer.
- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2017b. Metal matrix nanocomposites: An overview. In: *Aluminum and Magnesium Metal Matrix Nanocomposites*. Singapore: Springer.
- Dai, L.H., Ling, Z., Bai, Y.L., 2001a. Size-dependent inelastic behavior of particle-reinforced metal–matrix composites. *Composites Science and Technology* 61, 1057–1063.
- Darmiani, E., Danaee, I., Golozar, M.A., Toroghinejad, M.R., 2013. Corrosion investigation of Al–SiC nano-composite fabricated by accumulative roll bonding (ARB) process. *Journal of Alloys and Compounds* 552, 31–39.
- de Cicco, M.P., Li, X., Turng, L.-S., 2009. Semi-solid casting (SSC) of zinc alloy nanocomposites. *Journal of Materials Processing Technology* 209, 5881–5885.
- de Cicco, M.P., 2009. Solidification Phenomena in Metal Matrix Nanocomposites (PhD Thesis). University of Wisconsin.

- Donthamsetty, S., Damera, N., Jain, P., 2009. Ultrasonic cavitation assisted fabrication and characterization of A356 metal matrix nanocomposite reinforced with SiC, B4C, CNTs. *Asian International Journal of Science and Technology in Production and Manufacturing Engineering* 2, 27–34.
- Dunand, D., Mortensen, A., 1991. On plastic relaxation of thermal stresses in reinforced metals. *Acta Metallurgica et Materialia* 39, 127–139.
- Eskin, G.I., Eskin, D.G., 2014. *Ultrasonic Treatment of Light Alloy Melts*. CRC Press.
- Eskin, G.I., Eskin, D.G., 2015. *Ultrasonic Treatment of Light Alloy Melts*. CRC Press.
- Ghalebandi, S.M., Malaki, M., Gupta, M., 2019. Accumulative roll bonding – A review. *Applied Sciences* 9, 3627.
- Goh, C., Wei, J., Lee, L., Gupta, M., 2006. Simultaneous enhancement in strength and ductility by reinforcing magnesium with carbon nanotubes. *Materials Science and Engineering: A* 423, 153–156.
- Goh, C., Wei, J., Lee, L., Gupta, M., 2007. Properties and deformation behaviour of Mg–Y₂O₃ nanocomposites. *Acta Materialia* 55, 5115–5121.
- Goh, C., Wei, J., Lee, L., Gupta, M., 2008. Ductility improvement and fatigue studies in Mg–CNT nanocomposites. *Composites Science and Technology* 68, 1432–1439.
- Gong, H., Anasori, B., Dennison, C.R., *et al.*, 2015. Fabrication, biodegradation behavior and cytotoxicity of Mg–nanodiamond composites for implant application. *Journal of Materials Science: Materials in Medicine* 26, 110.
- Gupta, M., Wong, W., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.
- Gupta, M., Meenashisundaram, G.K., 2015. *Insight Into Designing Biocompatible Magnesium Alloys and Composites: Processing, Mechanical and Corrosion Characteristics*. Springer.
- Habibnejad-Korayem, M., Mahmudi, R., Poole, W.J., 2009. Enhanced properties of Mg-based nano-composites reinforced with Al₂O₃ nano-particles. *Materials Science and Engineering: A* 519, 198–203.
- Hall, E., 1951. The deformation and ageing of mild steel: III discussion of results. *Proceedings of the Physical Society. Section B* 64, 747.
- Hamedan, A.D., Shahmiri, M., 2012. Production of A356–1 wt% SiC nanocomposite by the modified stir casting method. *Materials Science and Engineering: A* 556, 921–926.
- Hashemi, M., Jamaati, R., Toroghinejad, M.R., 2012. Microstructure and mechanical properties of Al/SiO₂ composite produced by CAR process. *Materials Science and Engineering: A* 532, 275–281.
- Hassan, H.A., Lewandowski, J.J., 2014. Effects of particulate volume fraction on cyclic stress response and fatigue life of AZ91D magnesium alloy metal matrix composites. *Materials Science and Engineering: A* 600, 188–194.
- Hassan, H.A., Lewandowski, J.J., 2018. 4.4 Fracture toughness and fatigue of particulate metal matrix composites. *Comprehensive Composite Materials II* 4, 86–136.
- Hemanth, J., 2009. Development and property evaluation of aluminum alloy reinforced with nano-ZrO₂ metal matrix composites (NMMCs). *Materials Science and Engineering: A* 507, 110–113.
- Ho, K., Gupta, M., Srivatsan, T.S., 2004. The mechanical behavior of magnesium alloy AZ91 reinforced with fine copper particulates. *Materials Science and Engineering: A* 369, 302–308.
- Hsu, C., Kao, P., Ho, N., 2005. Ultrafine-grained Al–Al₂Cu composite produced in situ by friction stir processing. *Scripta Materialia* 53, 341–345.
- Hsu, C., Chang, C., Kao, P., Ho, N., Chang, C., 2006. Al–Al₃Ti nanocomposites produced in situ by friction stir processing. *Acta Materialia* 54, 5241–5249.
- Jamaati, R., Toroghinejad, M.R., 2010. High-strength and highly-uniform composite produced by anodizing and accumulative roll bonding processes. *Materials & Design* 31, 4816–4822.
- Jamaati, R., Amir Khanlou, S., Toroghinejad, M.R., Niroumand, B., 2011. Effect of particle size on microstructure and mechanical properties of composites produced by ARB process. *Materials Science and Engineering: A* 528, 2143–2148.
- Jamaati, R., Toroghinejad, M.R., Dutkiewicz, J., Szpunar, J.A., 2012. Investigation of nanostructured Al/Al₂O₃ composite produced by accumulative roll bonding process. *Materials & Design* 35, 37–42.
- Karimi, M., Toroghinejad, M.R., Dutkiewicz, J., 2016. Nanostructure formation during accumulative roll bonding of commercial purity titanium. *Materials Characterization* 122, 98–103.
- Khabushan, J.K., Bonabi, S.B., 2017. Investigating of the microstructure and mechanical properties of Al-based composite reinforced with nano-trioxide tungsten via accumulative roll bonding process. *Open Journal of Metal* 7, 9–23.
- Kim, C.-S., Sohn, I., Nezafati, M., *et al.*, 2013b. Prediction models for the yield strength of particle-reinforced unimodal pure magnesium (Mg) metal matrix nanocomposites (MMNCs). *Journal of Materials Science* 48, 4191–4204.
- Lee, C., Huang, J., Hsieh, P., 2006. Mg based nano-composites fabricated by friction stir processing. *Scripta Materialia* 54, 1415–1420.
- Lim, D.K., Shibayanagi, T., Gerlich, A.P., 2009. Synthesis of multi-walled CNT reinforced aluminium alloy composite via friction stir processing. *Materials Science and Engineering: A* 507, 194–199.
- Liu, C., Wang, Q., Jia, Y., *et al.*, 2012. Effect of W particles on the properties of accumulatively roll-bonded Al/W composites. *Materials Science and Engineering: A* 547, 120–124.
- Liu, C., Wang, Q., Jia, Y., *et al.*, 2013. Evaluation of mechanical properties of 1060-Al reinforced with WC particles via warm accumulative roll bonding process. *Materials & Design* 43, 367–372.
- Lloyd, D., 1994. Particle reinforced aluminium and magnesium matrix composites. *International Materials Reviews* 39, 1–23.
- Ly, Z., Ren, X., Hou, H., 2017. Application of accumulative roll bonding process for manufacturing Mg/2 wt% CNTs nanocomposite with superior mechanical properties. *Journal of Nanoscience and Nanotechnology* 17, 4022–4031.
- Malaki, M., Xu, W., Kasar, A.K., *et al.*, 2019. Advanced metal matrix nanocomposites. *Metals* 9, 330.
- Matli, P.R., Ubaid, F., Shakoob, R.A., *et al.*, 2017. Improved properties of Al–Si₃N₄ nanocomposites fabricated through a microwave sintering and hot extrusion process. *RSC Advances* 7, 34401–34410.
- Mazaheri, Y., Karimzadeh, F., Enayati, M., 2011. A novel technique for development of A356/Al₂O₃ surface nanocomposite by friction stir processing. *Journal of Materials Processing Technology* 211, 1614–1619.
- Morisada, Y., Fujii, H., Nagaoka, T., Fukusumi, M., 2006. MWCNTs/AZ31 surface composites fabricated by friction stir processing. *Materials Science and Engineering: A* 419, 344–348.
- Nardone, V.C., Prew, K.M., 1986. On the strength of discontinuous silicon carbide reinforced aluminum composites. *Scripta Metallurgica* 20, 43–48.
- Paul, W., Sharma, C.P., 2006. Nanoceramic matrices: Biomedical applications. *American Journal of Biochemistry and Biotechnology* 2, 41–48.
- Petch, N., 1953. The cleavage strength of polycrystals. *Journal of the Iron and Steel Institute* 174, 25–28.
- Ramakrishnan, N., 1996. An analytical study on strengthening of particulate reinforced metal matrix composites. *Acta Materialia* 44, 69–77.
- Redsten, A., Klier, E., Brown, A., Dunand, D., 1995. Mechanical properties and microstructure of cast oxide-dispersion-strengthened aluminum. *Materials Science and Engineering: A* 201, 88–102.
- Rozak, G., Lewandowski, J., Wallace, J., Altmisoglu, A., 1992. Effects of casting conditions and deformation processing on A356 aluminum and A356–20 vol% SiC composites. *Journal of Composite Materials* 26, 2076–2106.
- Saito, Y., Tsuji, N., Utsunomiya, H., Sakai, T., Hong, R., 1998. Ultra-fine grained bulk aluminum produced by accumulative roll-bonding (ARB) process. *Scripta Materialia* 39, 1221–1227.
- Sajjadi, S.A., Ezatpour, H., Beygi, H., 2011. Microstructure and mechanical properties of Al–Al₂O₃ micro and nano composites fabricated by stir casting. *Materials Science and Engineering: A* 528, 8765–8771.
- Sanaty-Zadeh, A., 2012. Comparison between current models for the strength of particulate-reinforced metal matrix nanocomposites with emphasis on consideration of Hall–Petch effect. *Materials Science and Engineering: A* 531, 112–118.

- Shafiei-Zarghani, A., Kashani-Bozorg, S., Zarei-Hanzaki, A., 2009. Microstructures and mechanical properties of Al/Al₂O₃ surface nano-composite layer produced by friction stir processing. *Materials Science and Engineering: A* 500, 84–91.
- Sharifitabar, M., Sarani, A., Khorshahian, S., Afarani, M.S., 2011. Fabrication of 5052Al/Al₂O₃ nanoceramic particle reinforced composite via friction stir processing route. *Materials & Design* 32, 4164–4172.
- Shin, S.E., Bae, D.H., 2018. Fatigue behavior of Al2024 alloy-matrix nanocomposites reinforced with multi-walled carbon nanotubes. *Composites Part B: Engineering* 134, 61–68.
- Simões, S., Viana, F., Reis, M.A., Vieira, M.F., 2017. Aluminum and nickel matrix composites reinforced by CNTs: Dispersion/mixture by ultrasonication. *Metals* 7, 279.
- Soltani, M.A., Jamaati, R., Toroghinejad, M.R., 2012. The influence of TiO₂ nano-particles on bond strength of cold roll bonded aluminum strips. *Materials Science and Engineering: A* 550, 367–374.
- Srivatsan, T., Godbole, C., Paramsothy, M., Gupta, M., 2012. Influence of nano-sized carbon nanotube reinforcements on tensile deformation, cyclic fatigue, and final fracture behavior of a magnesium alloy. *Journal of Materials Science* 47, 3621–3638.
- Srivatsan, T., Godbole, C., Quick, T., Paramsothy, M., Gupta, M., 2013. Mechanical behavior of a magnesium alloy nanocomposite under conditions of static tension and dynamic fatigue. *Journal of materials engineering and performance* 22, 439–453.
- Suárez, S., Reinert, L., Mücklich, F., 2016. Carbon nanotube (CNT)-reinforced metal matrix bulk composites: Manufacturing and evaluation. In *Diamond and Carbon Composites and Nanocomposites*. InTech.
- Suresh, S., 2013. *Fundamentals of Metal-Matrix Composites*. Elsevier.
- Suresh, S., Mishra, D., Srinivasan, A., Arunachalam, R., Sasikumar, R., 2011. Production and characterization of micro and nano Al₂O₃ particle-reinforced LM25 aluminium alloy composites. *ARPN Journal of Engineering and Applied Sciences* 6, 94–98.
- Suryanarayana, C., 2001. Mechanical alloying and milling. *Progress in Materials Science* 46, 1–184.
- Suryanarayana, C., 2011. Synthesis of nanocomposites by mechanical alloying. *Journal of Alloys and Compounds* 509, S229–S234.
- Suryanarayana, C., Al-Aqeeli, N., 2013. Mechanically alloyed nanocomposites. *Progress in Materials Science* 58, 383–502.
- van Pham, T., Bui, H.T., Tran, B.T., *et al.*, 2011. The effect of sintering temperature on the mechanical properties of a Cu/CNT nanocomposite prepared via a powder metallurgy method. *Advances in Natural Sciences: Nanoscience and Nanotechnology* 2, 015006.
- Vogt, R., Zhang, Z., Li, Y., *et al.*, 2009. The absence of thermal expansion mismatch strengthening in nanostructured metal–matrix composites. *Scripta Materialia* 61, 1052–1055.
- Wang, Z.H., Kang, Y.L., Zhao, H.J., Xu, Y., 2006. SiC nanoparticles reinforced magnesium alloys by semisolid process. In *Solid State Phenomena*. Trans Tech Publ. pp. 163–166.
- Xia, J., Lewandowski, J.J., Willard, M.A., 2019. Tension and fatigue behavior of Al-2124A/SiC-particulate metal matrix composites. *Materials Science and Engineering: A*. 138518.
- Yang, M., Xu, C., Wu, C., *et al.*, 2010. Fabrication of AA6061/Al₂O₃ nano ceramic particle reinforced composite coating by using friction stir processing. *Journal of Materials Science* 45, 4431–4438.
- Yazdani, A., Salahinejad, E., 2011. Evolution of reinforcement distribution in Al–B₄C composites during accumulative roll bonding. *Materials & Design* 32, 3137–3142.
- Ye, J., Lee, Z., Ahn, B., *et al.*, 2006. Cryomilling for the fabrication of a particulate B₄C reinforced Al nanocomposite: Part II. Mechanisms for microstructural evolution. *Metallurgical and Materials Transactions A* 37, 3111–3117.
- Zhang, Q., Xiao, B., Wang, Q., Ma, Z., 2011. In situ Al₃Ti and Al₂O₃ nanoparticles reinforced Al composites produced by friction stir processing in an Al-TiO₂ system. *Materials Letters* 65, 2070–2072.
- Zhang, Z., Chen, D., 2006. Consideration of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites: A model for predicting their yield strength. *Scripta Materialia* 54, 1321–1326.
- Zhang, Z., Chen, D., 2008. Contribution of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites. *Materials Science and Engineering: A* 483, 148–152.
- Zhong, X.L., Wong, W.L.E., Gupta, M., 2007. Enhancing strength and ductility of magnesium by integrating it with aluminum nanoparticles. *Acta Materialia* 55, 6338–6344.

An Insight Into Magnesium Based Metal Matrix Composites With Hybrid Reinforcement

Sankaranarayanan Seetharaman, National University of Singapore, Singapore

Subramanian Jayalakshmi and Ramachandra Arvind Singh, Wenzhou University, Wenzhou, China

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Magnesium, being the lightest structural metal is an excellent candidate for weight critical applications (Avedesian and Baker, 1999; Pekguleryuz *et al.*, 2013). Although magnesium (Mg) exhibits some of the interesting attributes such as low density, high specific resistance, good castability, and excellent machinability, its application in pure form is limited due to the inherent limitations such as poor absolute strength, deformability and corrosion susceptibility (Mordike and Ebert, 2001). While the alloy making with Al, Zn, Zr, and RE additions tends to overcome most of these limitations, the specific stiffness and strength properties are improved by introducing the desired amount of ceramic reinforcements in the form of fibers or particles (Kainer *et al.*, 2010). Extensive researches have been conducted in this regard to develop new light weight Mg alloys and their composites (Gupta and Sharon, 2010; Sankaranarayanan and Gupta, 2015a).

In general, the thermally stable reinforcement phases act as nucleation sites for Mg-grains and introduce stress fields due to a mismatch in thermal expansion behavior (Ibrahim *et al.*, 1991; Srivatsan *et al.*, 1995; Malaki *et al.*, 2019). Both the effects inhibit the dislocation motion to result in better strength properties. Recently, the use of nanoscale ceramic particles also received extensive attention owing to their dispersion strengthening benefits (Gupta and Wong, 2015; Sankaranarayanan and Gupta, 2015; Malaki *et al.*, 2019). In most reports, the incorporation of dilute volume fraction of nano-sized reinforcements also enhanced the ductility unlike the micron sized particles or fibers. Similar benefits were also reported for metallic reinforcements with limited/no solubility in Mg (Hassan and Gupta, 2002; Wong and Gupta, 2007; Fida Hassan *et al.*, 2015b).

Some of the published literature in open public domain also report the positive influence of hybrid reinforcements in improving the mechanical properties of Mg (Ugandhar *et al.*, 2006; Habibi *et al.*, 2011; Sankaranarayanan *et al.*, 2011b, 2013; Rashad *et al.*, 2015b; Sahoo *et al.*, 2018). In some of these studies, the hybrid reinforcements were also pre-processed using solid state powder techniques like ball-milling and the end properties of MMCs were strongly influenced by factors such as: the type of processing methods, the matrix and reinforcement constituents, the shape and volume fraction of the reinforcements and the method of reinforcement preparation (Sankaranarayanan *et al.*, 2011b).

In view of this, an attempt is made in this article to document the properties of magnesium-based metal matrix composites containing hybrid reinforcement placing special emphasis on the processing methods.

Melt Infiltration and Squeeze Casting of Magnesium Composites Containing Hybrid Reinforcements

The idea of hybrid (fiber + particle) reinforcement addition to Mg matrix was first proposed by Schröder and Kainer (1991) as an economical alternative to expensive ceramic fibers. Here, the Mg hybrid composites were fabricated by the liquid metal infiltration of preforms containing Al_2O_3 short fibers and SiC particles using a high temperature Mg-2.5Ag-2RE-0.6Zr alloy as the matrix material (as illustrated in Fig. 1). The developed hybrid composites were rationalized with lower costs and more isotropic properties (Fig. 2) compared with fiber reinforced composites produced using squeeze casting methods.

Asano and Yoneda (2008a,b) also used the infiltration technique to investigate the effect of Si addition on the properties of Saffil short fibers reinforced AZ91D composites. While the reaction between Si particles and molten Mg results in the in-situ formation of Mg_2Si particles (as illustrated in Fig. 3), the introduction of red phosphorous (P) or CaF_2 promoted the refinement of Mg_2Si particles. Further, the composites showed better tensile strength for in-situ Mg_2Si particle reinforced Saffil fibers/AZ91D composites in the temperature range from 293K to 523K (Fig. 4).

In a similar study (Babu *et al.*, 2010), AM50 alloy-based Mg composites containing Al_2O_3 short fibers and graphite nano-fibers (GNF) were produced using the melt-infiltration technique. The results of mechanical characterization in this study (Fig. 5) showed improvement in hardness, tensile strength, and compressive strength of composites up to a threshold of 10% volume fraction GNF. However, beyond 10 vol%, agglomeration of GNFs occurred (Fig. 6). In another study (Babu and Kang, 2010), the same authors, reported the nanomechanical properties of AM50/ Al_2O_3 /sf-GNF hybrid composites based on continuous stiffness measurements (CSM). The comparison of measurements from different locations such as GNFs/ Al_2O_3 /sf region, Al_2O_3 /sf region, GNFs cluster, and Mg matrix showed relatively larger modulus and hardness values at the GNFs/ Al_2O_3 /sf interface (Table 1).

Kumar *et al.* (2005, 2007) also used the squeeze casting method to develop AE42 alloy based hybrid composites reinforced with Saffil short fibers and SiC particles. The developed composites were investigated for various properties including thermal cycling, impression creep, sliding wear and corrosion. While the results of thermal cycling studies showed a reduction in the CTE

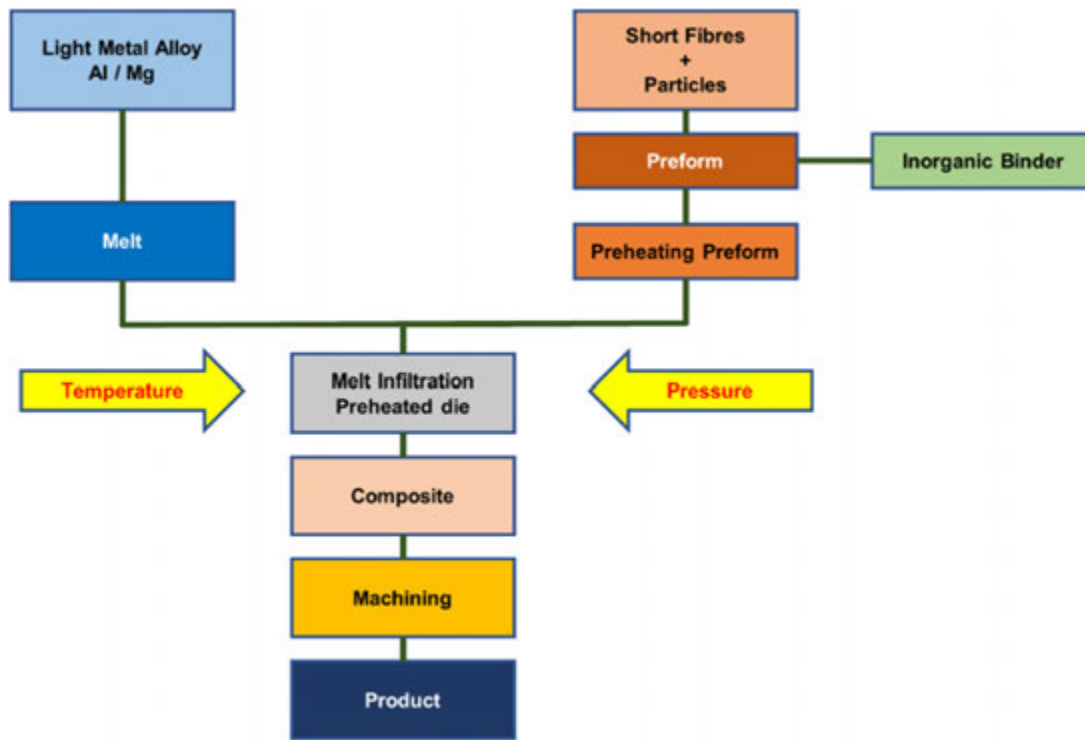


Fig. 1 Melt infiltration of Mg hybrid composites. Modified from Schröder, J., Kainer, K.U., 1991. Magnesium-base hybrid composites prepared by liquid infiltration. Materials Science and Engineering A. 135, 33–36. Available at: [https://doi.org/10.1016/0921-5093\(91\)90532-R](https://doi.org/10.1016/0921-5093(91)90532-R).

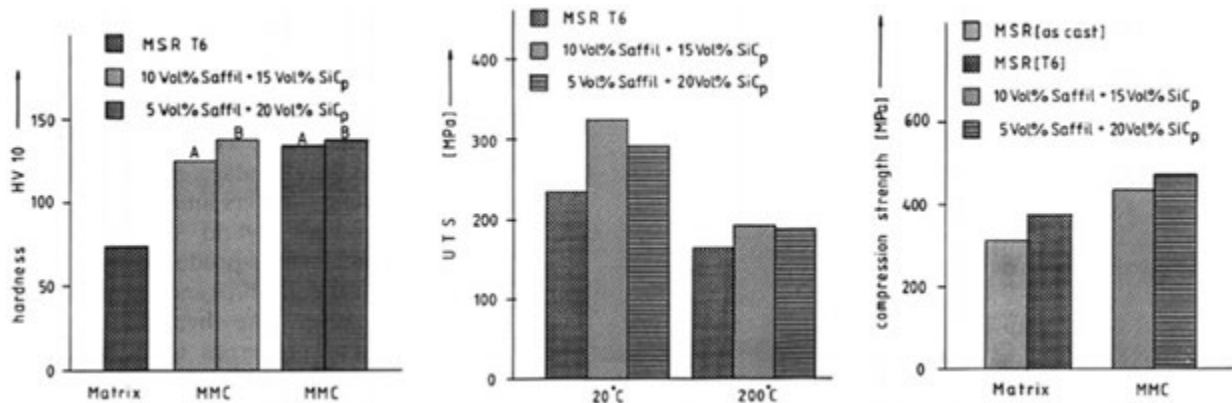


Fig. 2 Mechanical properties of Mg based Composites reinforced with Saffil fibers and SiC particles reported by Modified from Schröder, J., Kainer, K.U., 1991. Magnesium-base hybrid composites prepared by liquid infiltration. Materials Science and Engineering A. 135, 33–36. Available at: [https://doi.org/10.1016/0921-5093\(91\)90532-R](https://doi.org/10.1016/0921-5093(91)90532-R).

values with increasing amounts of SiC particles, the experimental values along the transverse direction showed a positive deviation from linearity above 215°C as shown in Table 2. The same was attributed to the relaxation of residual compressive strain from the squeeze casting process (Kumar *et al.*, 2005, 2007). This study also highlighted the complex interaction between the Saffil short fibers and SiC particles resulting in a much reduced CTE value when compared to the calculated ones assuming a simple rule of mixture.

In a different study, the same group reported the impression creep response of AE42/Saffil fibers-SiC composites (Mondal and Kumar, 2008, 2009b). The results highlighted a normal creep behavior (i.e., strain rate decreasing with strain and then reaching a steady state) of developed hybrid composites at all the stresses employed at 175°C, and up to 80 MPa stress at 240°C (Fig. 7). However, above 80 MPa at 240°C, the creep behavior was found to be reverse (i.e., strain rate increasing with strain, then reaching a steady state and then decreasing). Similar reverse creep behavior associated with fiber breakage was also reported for all the stress levels at 300°C. Based on the calculated true stress exponent values, the dominant creep mechanisms

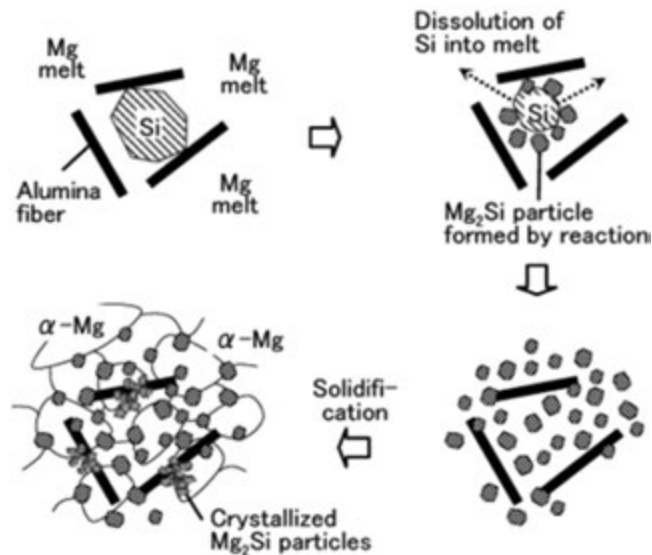


Fig. 3 Schematic explanation of the formation and dispersion of Mg_2Si particles. Reproduced from Asano, K., Yoneda, H., 2008a. Development of short alumina fibre and in situ Mg_2Si particle reinforced magnesium alloy hybrid composite with high temperature strength. International Journal of Cast Metals Research 21 (1-4), 239–245. Available at: <https://doi.org/10.1179/136404608X362025>. Asano, K., Yoneda, H., 2008b. High temperature properties of AZ91D magnesium alloy composite reinforced with short alumina fiber and Mg_2Si particle. Materials Transactions 49 (7), 1688–1693. Available at: <https://doi.org/10.2320/matertrans.MER2008092>.

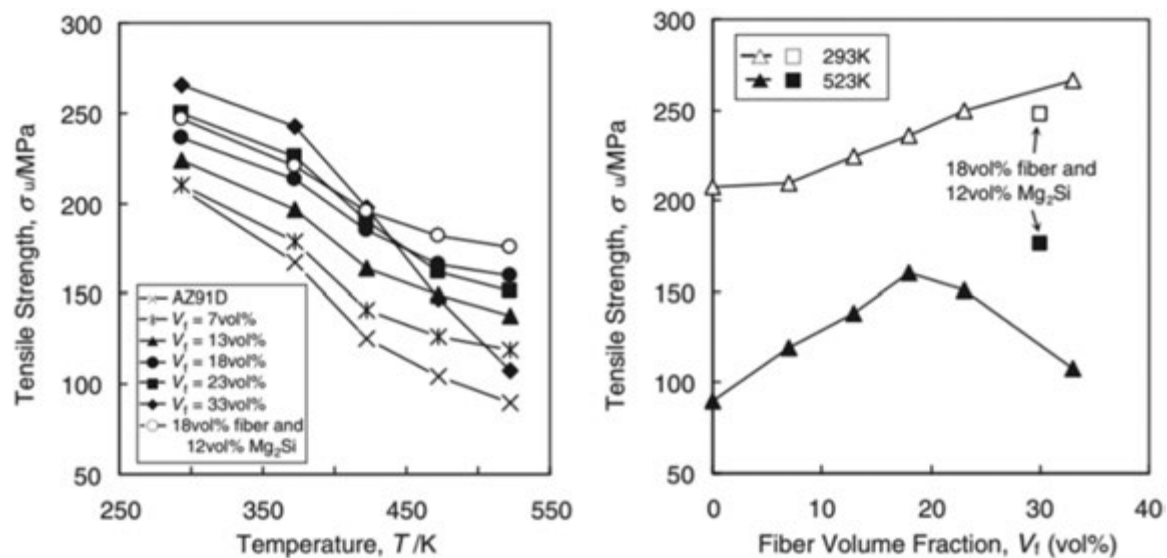


Fig. 4 Effect of temperature and reinforcement volume fraction on the tensile strength of Saffil short fibers and Mg_2Si particles reinforced AZ91D composites. Reproduced from Asano, K., Yoneda, H., 2008a. Development of short alumina fibre and in situ Mg_2Si particle reinforced magnesium alloy hybrid composite with high temperature strength. International Journal of Cast Metals Research 21 (1-4), 239–245. Available at: <https://doi.org/10.1179/136404608X362025>. Asano, K., Yoneda, H., 2008b. High temperature properties of AZ91D magnesium alloy composite reinforced with short alumina fiber and Mg_2Si particle. Materials Transactions 49 (7), 1688–1693. Available at: <https://doi.org/10.2320/matertrans.MER2008092>.

of developed hybrid composites were reported as viscous glide and dislocation climb. While the creep rate of all the composites was generally higher in transverse direction compared to the longitudinal direction, the hybrid composites exhibited comparable creep resistance as that of the composite containing only Saffil short fibers. Improvement in creep properties due to hybrid reinforcements was also reported by Svoboda *et al.* (2007) in case of a squeeze cast AZ91 composite reinforced with 7 vol % short carbon fibers and 15 vol% SiC particulates (Fig. 8). However, the same study also reported no benefits due to hybrid (carbon fiber + SiC particles) reinforcement for QE22 matrix alloy.

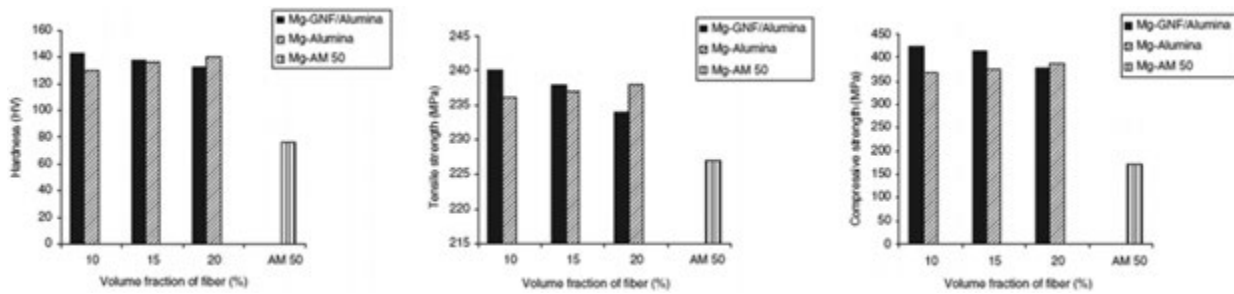


Fig. 5 Mechanical properties of Al₂O₃ short fibers and graphite nanofibers reinforced AM50 composites. Reproduced from Babu, J.S.S., *et al.*, 2010. Fabrication and properties of magnesium (AM50)-based hybrid composites with graphite nanofiber and alumina short fiber. Journal of Composite Materials 44 (8), 971–987. Available at: <https://doi.org/10.1177/0021998309349548>.

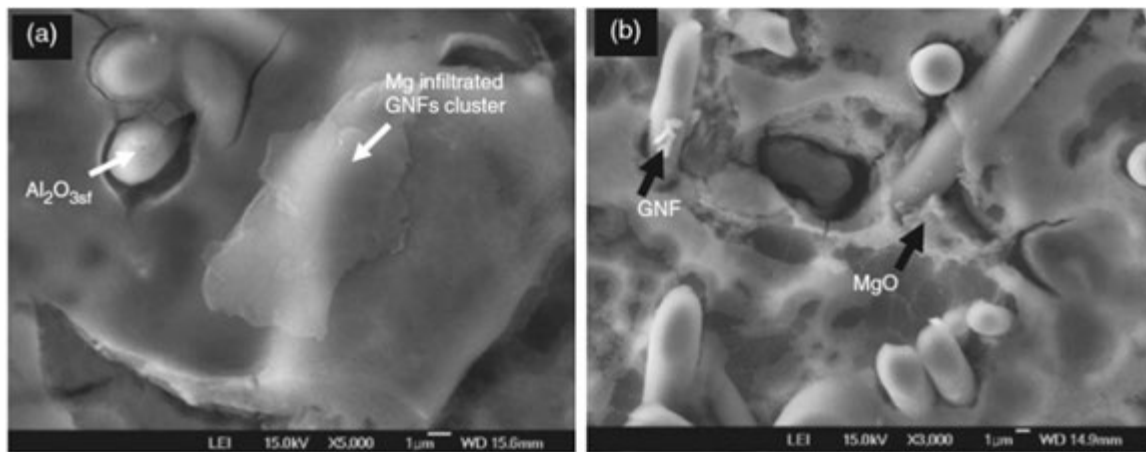


Fig. 6 (a) Mg infiltrated GNF clusters, (b) showing individual GNF stick on the surface of Al₂O_{3sf} and highly deposited MgO along the surface of Al₂O_{3sf}. Reproduced from Babu, J.S.S., *et al.*, 2010. Fabrication and properties of magnesium (AM50)-based hybrid composites with graphite nanofiber and alumina short fiber. Journal of Composite Materials 44 (8), 971–987. Available at: <https://doi.org/10.1177/0021998309349548>.

Table 1 Modulus and hardness reports of Mg/Al₂O_{3sf}-CNFcomposites reported by Babu *et al.*

Location	Longitudinal section		Transverse section	
	Modulus (GPa)	Hardness (GPa)	Modulus (GPa)	Hardness (GPa)
Mg-matrix	76	1.8	76	1.3
Al ₂ O _{3sf}	80	1.2	85	1.4
GNF/Al ₂ O _{3sf} interface	130	3	90	1.7
GNF Cluster	85	1.5	84	1.3

Note: Babu, J.S.S., *et al.*, 2010. Fabrication and properties of magnesium (AM50)-based hybrid composites with graphite nanofiber and alumina short fiber. Journal of Composite Materials 44 (8), 971–987. Available at: <https://doi.org/10.1177/0021998309349548>.

Table 2 Theoretical and experimental average CTE values of AE42 composites in the temperature range 20–200°C

Materials	Theoretical CTE (µ/K)	Corrected Experimental CTE in LD (µ/K)	Corrected Experimental CTE in TD (µ/K)
AE42	27.1	27.1	27.1
AE42/20Saffil	26.6	18.2	21.8
AE42/15Saffil-5SiC	26.1	18.3	22.5
AE42/15Saffil-10SiC	25.4	17.6	22.2
AE42/15Saffil-15SiC	24.2	14.0	20.3

Note: Kumar, S., Dieringa, H., Kainer, K.U., 2005. Effect of particulate content on the thermal cycling behaviour of the magnesium alloy based hybrid composites. Composites Part A Applied Science and Manufacturing 36 (3), 321–325. Available at: <https://doi.org/10.1016/j.compositesa.2004.07.005>. Kumar, S., Dieringa, H., Kainer, K.U., 2007. Thermal cycling behaviour of the magnesium alloy based hybrid composites in the transverse direction. Materials Science and Engineering A 454–455, 367–370. Available at: <https://doi.org/10.1016/j.msea.2006.11.041>.

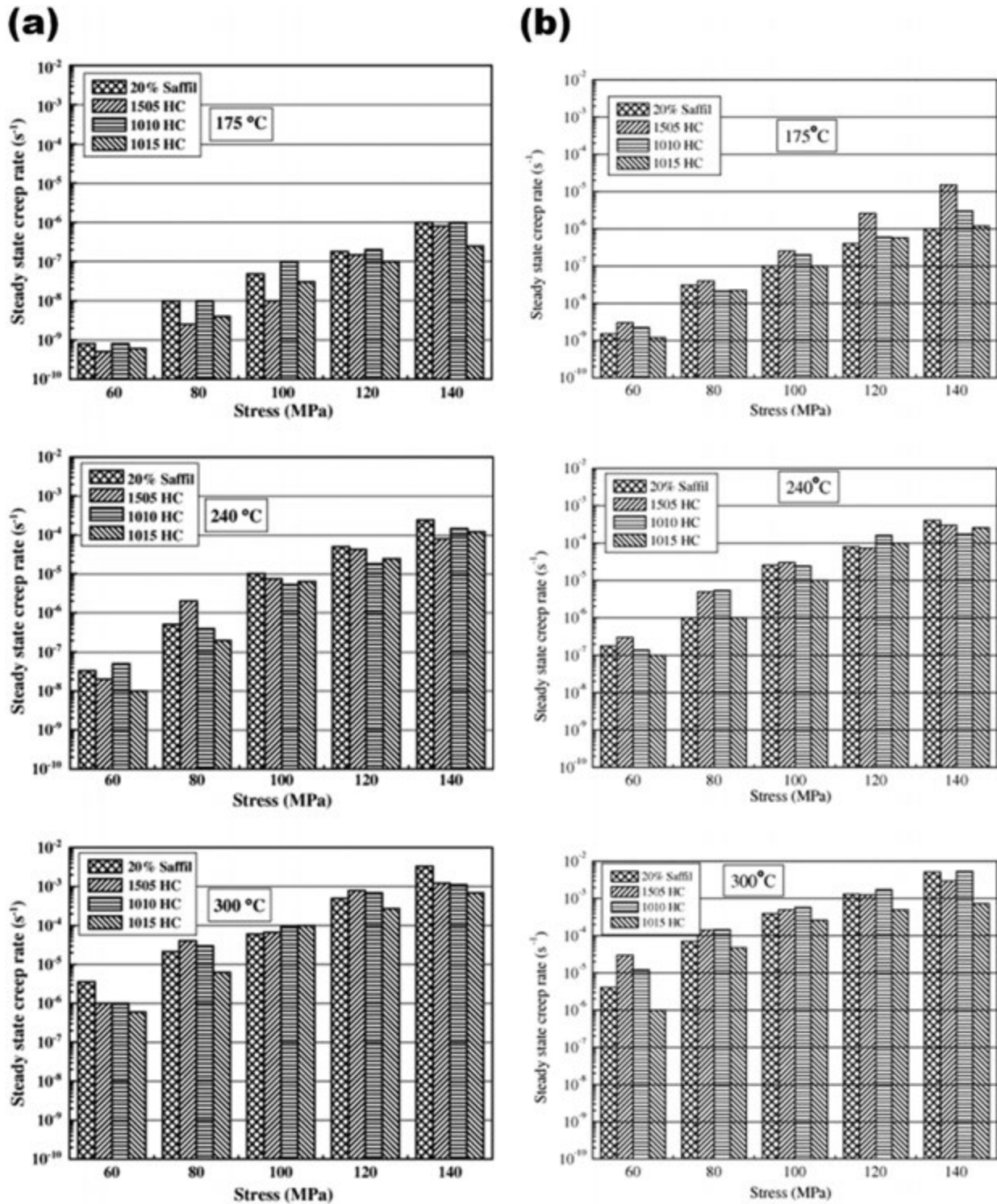


Fig. 7 Impression creep response of AE42/Saffil-SiC hybrid composites at temperatures (a) along the longitudinal and (b) transverse direction. Reproduced from Mondal, A.K., Kumar, S., 2008. Impression creep behaviour of magnesium alloy-based hybrid composites in the longitudinal direction. *Composites Science and Technology* 68 (15-16), 3251–3258. Available at: <https://doi.org/10.1016/j.compscitech.2008.08.007>. Mondal, A. K., Kumar, S., 2009b. Impression creep behaviour of magnesium alloy-based hybrid composites in the transverse direction. *Composites Science and Technology* 69 (10), 1592–1598. Available at: <https://doi.org/10.1016/j.compscitech.2009.02.038>.

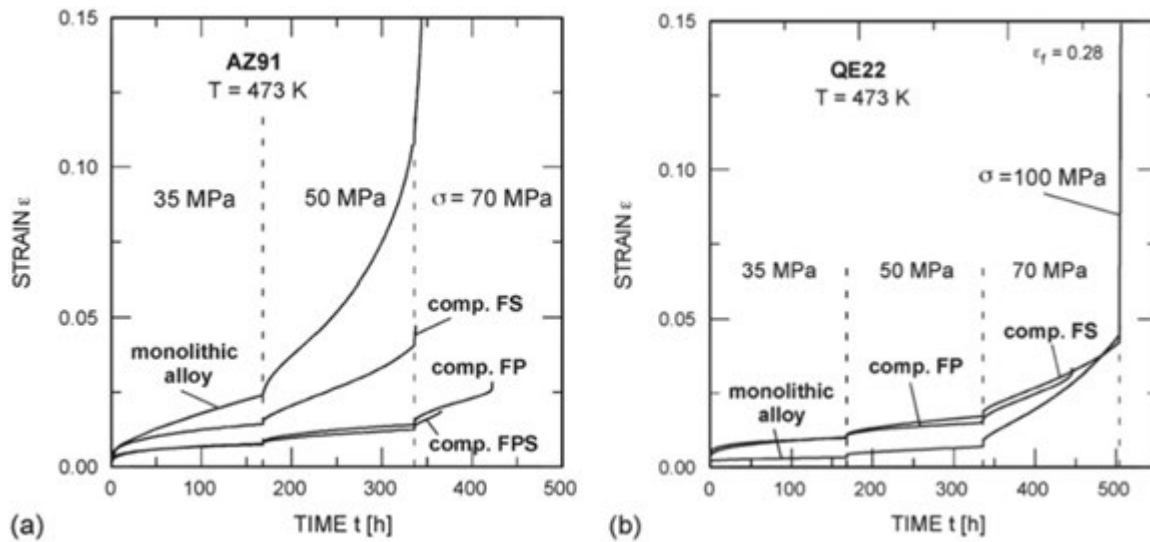


Fig. 8 Creep curves for (a) AZ91 and (b) QE based hybrid composites reinforced with (fiber + silicon, FS), (fiber + particles, FP), and (fiber + particles + silicon, FPS). Reproduced from Svoboda, M., *et al.*, 2007. Microstructure and creep behaviour of magnesium hybrid composites. Materials Science and Engineering A 562 (1-2), 220–224. Available at: <https://doi.org/10.1016/j.msea.2006.02.466>.

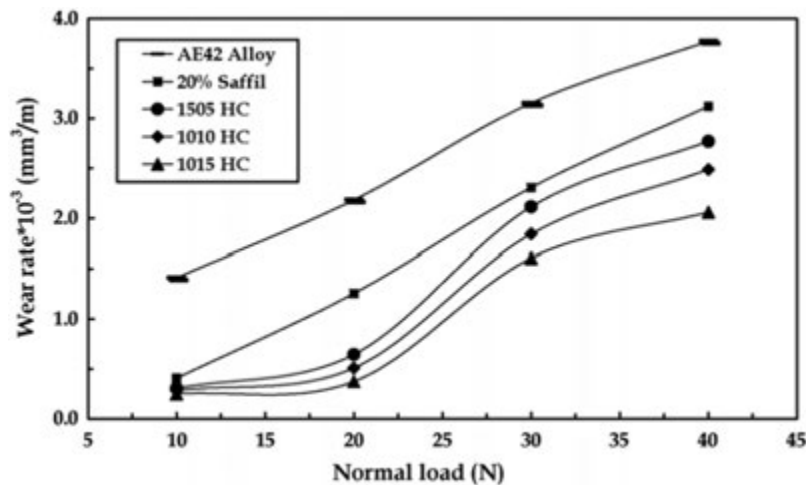


Fig. 9 Volumetric wear rate of AE42 alloy composites reported by Mondal and Kumar. Reproduced from Mondal, A.K., Kumar, S., 2009a. Dry sliding wear behaviour of magnesium alloy based hybrid composites in the longitudinal direction. Wear 267 (1-4), 458–466. Available at: <https://doi.org/10.1016/j.wear.2008.12.036>. Mondal, A.K., Kumar, S., 2014. Dry sliding wear behaviour of magnesium alloy based hybrid composites in transverse direction. Materials Science Forum (783-786), 1530. Available at: <https://doi.org/10.4028/www.scientific.net/msf.783-786.1530>.

Mondal and Kumar (2009a, 2014) also investigated the dry sliding characteristics using a pin-on-disc set up at a constant sliding distance and sliding velocity, 2.5 km and 0.837 m/s respectively, for the load range 10–40 N. While the results showed an increase in the wear rate with respect to the applied load, the hybrid composites exhibited lower wear rate at all the loads when compared to the AE42 matrix alloy and the composite reinforced with only Saffil short fibers (Fig. 9). From the microstructural observations, the authors also confirmed the dominant wear mechanism as abrasion in all the materials as the worn-out surface of composites displayed fractured Saffil short fibers in addition to the severe plastic deformation of the surface layers. Further, in case of the hybrid composite, the micrographs showed intact SiC particles with significant amount of iron which confirmed the formation of an iron-rich transfer layer to delay the fracture of Saffil short fibers even at the highest load employed (Fig. 10).

The same authors (Mondal *et al.*, 2015) also reported the corrosion behavior of AE42 hybrid composites containing Saffil short fibers and SiC particles in various combinations. In this study, the composite containing Saffil short fiber alone exhibited a slightly better corrosion resistance when compared to the hybrid composites containing both Saffil short fibers and SiC particles. However, there was no specific trend reported on the SiC particle content and the poor corrosion resistance of the composites was attributed to the irregular and loose surface films (Fig. 11).

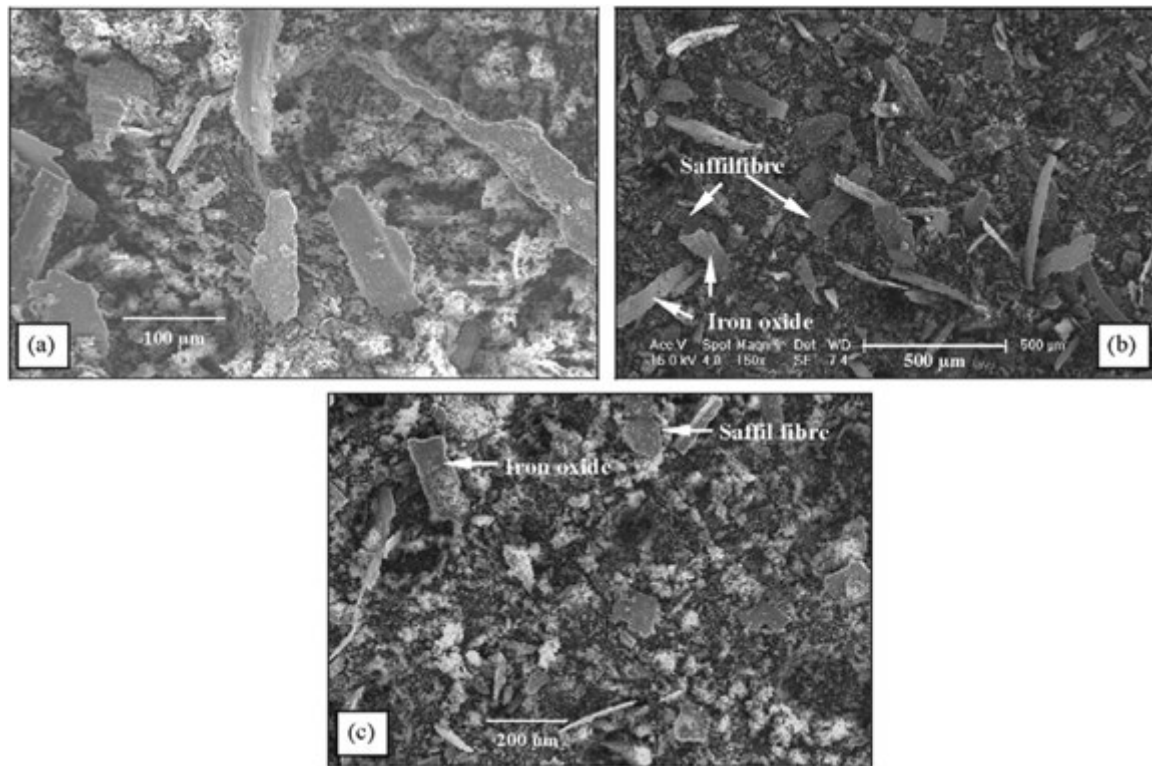


Fig. 10 SEM micrographs of the wear debris generated at 40N load for the (a) AE42 alloy; (b) 20% Saffil composite and (c) 1015 HC (Reported by Mondal and Kumar). Reproduced from Mondal, A.K., Kumar, S., 2009a. Dry sliding wear behaviour of magnesium alloy based hybrid composites in the longitudinal direction. Wear 267 (1-4), 458–466. Available at: <https://doi.org/10.1016/j.wear.2008.12.036>. Mondal, A.K., Kumar, S., 2014. Dry sliding wear behaviour of magnesium alloy based hybrid composites in transverse direction. Materials Science Forum (783-786), 1530. Available at: <https://doi.org/10.4028/www.scientific.net/msf.783-786.1530>.

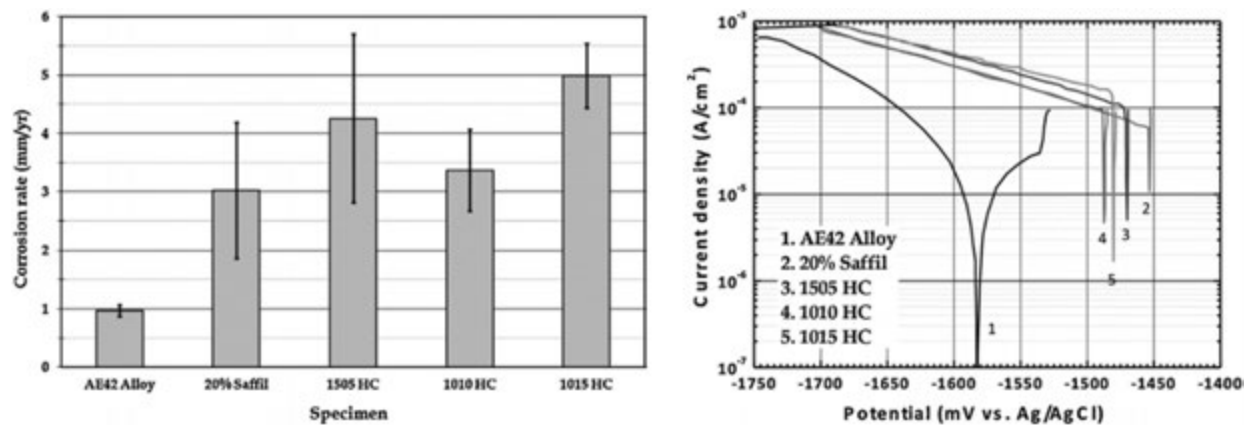


Fig. 11 Comparison of the corrosion rate of the AE42 alloy and its composites. Reproduced from Mondal, A.K., Blawert, C., Kumar, S., 2015. Corrosion behaviour of creep-resistant AE42 magnesium alloy-based hybrid composites developed for powertrain applications. Materials and Corrosion 6 (10), 1150–1158. Available at: <https://doi.org/10.1002/maco.201408071>.

In a similar study, the squeeze cast AM60 based composites containing Al_2O_3 reinforcements in the form of fibers and / or particles were investigated for the mechanical behavior and microstructure (Zhang *et al.*, 2014). The results showed an improvement in the hardness and the tensile strength of Mg composites due to the addition of Al_2O_3 fibers and/or particle reinforcement. In particular, the yield strength and the elastic modulus of the hybrid composite were $\sim 88\%$ and $\sim 40\%$ higher than that of the matrix alloy (Fig. 12). However, the ductility was compromised when compared to the unreinforced AM60 matrix alloy. Similarly, the microstructural studies also revealed significant grain refinement due to the hybrid reinforcement addition.

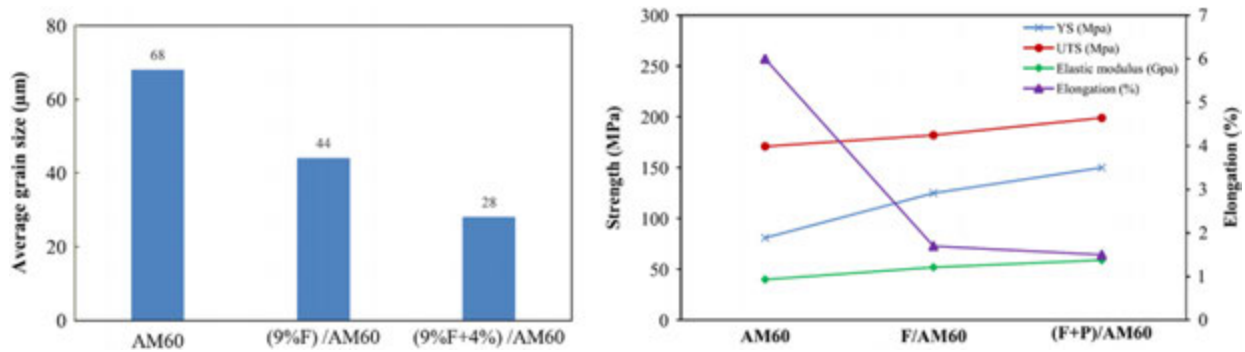


Fig. 12 Microstructure and mechanical properties of AM60 hybrid composites reported by Zhang *et al.* Reproduced from Zhang, X., Zhang, Q., Hu, H., 2014. Tensile behaviour and microstructure of magnesium AM60-based hybrid composite containing Al_2O_3 fibres and particles. Materials Science and Engineering A 607, 269–276. Available at: <https://doi.org/10.1016/j.msea.2014.03.069>.

Table 3 Mechanical properties of AM alloy-based hybrid composites reinforced with Al_2O_3 fibers and AlN or Al_2O_3 nanoparticles

Material	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)	Modulus (GPa)
AM60	81 ± 6	171 ± 8	6.0 ± 1.3	40 ± 4
AM60/ Al_2O_3 fibers	120 ± 5	189 ± 12	2.2 ± 1.7	50 ± 2
AM60/ Al_2O_3 nanoparticles	142 ± 7	192 ± 15	1.6 ± 1.1	54 ± 5
AM60/ Al_2O_3 fibers + nanoparticles	140 ± 14	216 ± 5	3.5 ± 1.2	53 ± 3
AM60/ Al_2O_3 fibers + n-AlN	139 ± 12	210 ± 7	3.6 ± 0.6	51 ± 4

Note: Zhou, J., *et al.*, 2017. Processing and properties of as-cast magnesium AM60-based composite containing alumina nano particles and micron fibres. Minerals, Metals and Materials Series. Available at: https://doi.org/10.1007/978-3-319-52392-7_79. Zhou, J., *et al.*, 2019a. As-cast magnesium AM60-based hybrid nanocomposite containing alumina fibres and nanoparticles: Microstructure and tensile behavior. Materials Science and Engineering A 740–741, 305–314. Available at: <https://doi.org/10.1016/j.msea.2017.10.070>.

Recently, Zhou *et al.* (Zhou *et al.*, 2017; Zhou *et al.*, 2019a) also devised a squeeze casting variant to develop AM60 based hybrid composites containing Al_2O_3 reinforcements in the form of fibers and particles. Since the aim of this study is to understand the effects of Al_2O_3 particle size, the hybrid composites were fabricated using Al_2O_3 fibers in combination with either micron or nano sized Al_2O_3 particles and the developed hybrid composites were investigated for their microstructure and mechanical properties. While the addition of Al_2O_3 reinforcements in the form of fibers and micron-sized particles considerably increased the ultimate tensile and yield strengths of the matrix alloy, the ductility was reduced substantially (Table 3). However, the addition of nano-sized Al_2O_3 particles (3 vol%) restored the ductility partially for the hybrid composite. Similar observations were also recorded when the nanosized Al_2O_3 particles were replaced by nanosized AlN particles.

Stir Casting and Friction Stir Processing of Magnesium Composites Containing Hybrid Reinforcements

AZ91D alloy based MMC containing boron carbide and graphite particle reinforcement were fabricated using the conventional stir casting method (Aatthisugan *et al.*, 2017). Here, the effects of graphite reinforcement were studied by comparing the mechanical and tribological of AZ91D/ B_4C -Gr hybrid composite with that of the AZ91D matrix alloy and AZ91D/ B_4C composite containing only B_4C particles. While the addition of B_4C particles to AZ91D alloy monotonically increased the wear resistance, hardness and tensile strength, the wear resistance and strength properties were found to degrade upon graphite addition in the case of AZ91D/ B_4C -Gr hybrid composites, although better than the AZ91D matrix alloy (Fig. 13).

Zhou *et al.* (2012) used the ultrasonic cavitation assisted semisolid stirring to fabricate AZ91 based hybrid composites containing different amounts of carbon nanotubes (CNTs) and silicon carbide (SiC) nanoparticles. The developed hybrid composites displayed a refined microstructure and improved mechanical properties due to hybrid reinforcement addition (Fig. 14). In particular, the tensile and yield strengths were significantly improved by ~45% and 55% respectively when the mass ratio between CNT and SiC nanoparticles was maintained as 7:3 (Fig. 15).

Arokiasamy and Anand Ronald (2017, 2018) investigated the influence of friction stir processing (FSP, as illustrated in Fig. 16) on the properties of Mg hybrid composites reinforced with SiC and Al_2O_3 particles. The results of microstructural studies showed appreciable refinement in grain size from 84 to 7 μm due to heterogenous nucleation of primary Mg grains during friction stir processing. With respect to mechanical properties, an improvement in microhardness from 59.3 Hv to 69.7 Hv due to friction stir surface processing was reported. However, the wear rate was found to increase generally for FSP composites (except sample code FSP 2) when compared to as-cast hybrid composites. The processing details and results from this study are listed in Table 4.

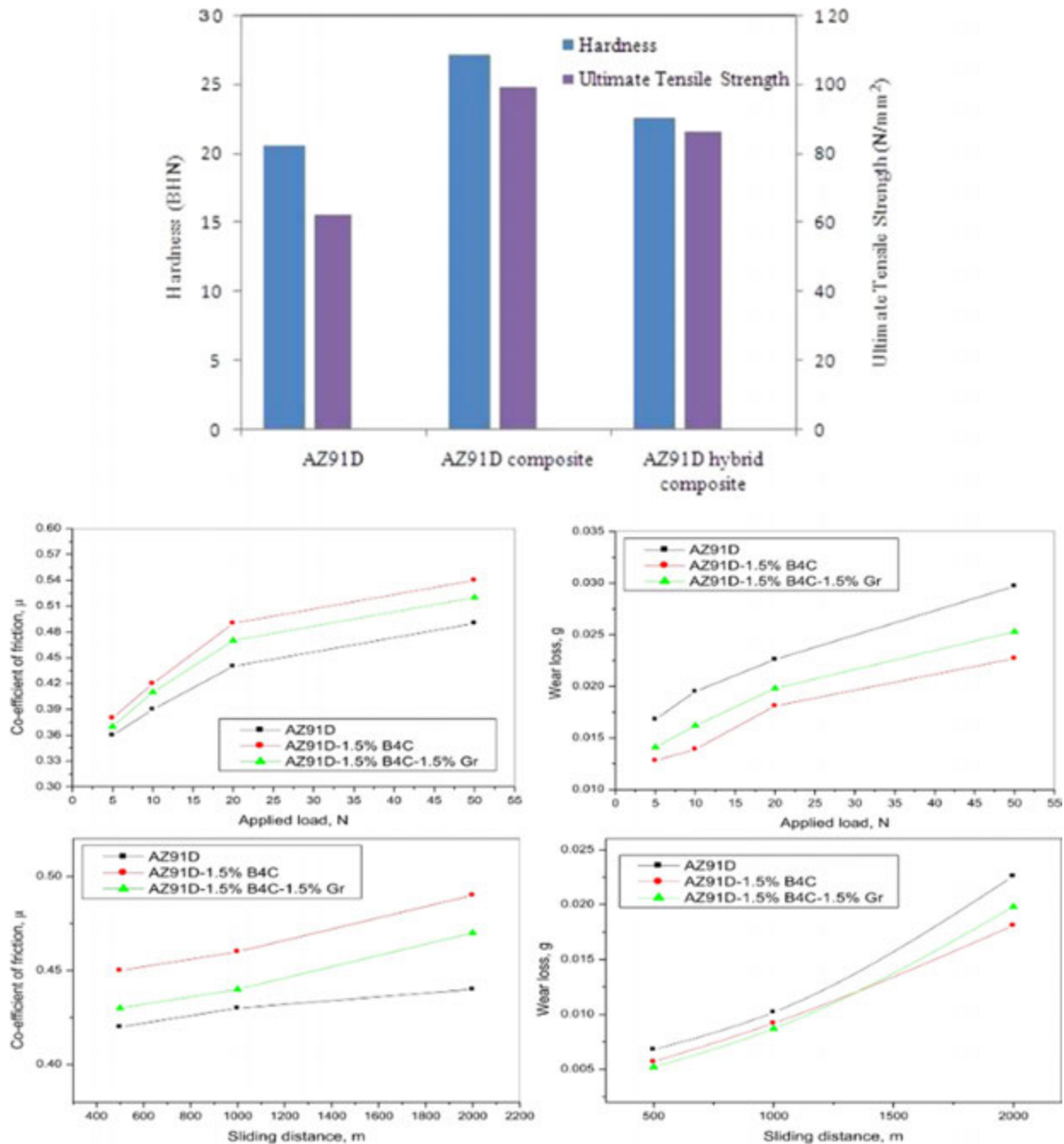


Fig. 13 Mechanical and Tribological properties of AZ91D/SiC-Gr hybrid composites. Reproduced from Aatthisugan, I., Razal Rose, A., Selwyn, D., 2017. Jeadurai Mechanical and wear behaviour of AZ91D magnesium matrix hybrid composite reinforced with boron carbide and graphite. Journal of Magnesium and Alloys 93, 493–503. Available at: <https://doi.org/10.1016/j.jma.2016.12.004>.

Sharma *et al.* (2019) also investigated the influence of FSP tool rotation speed on the properties of AZ61/CNT-GNP (graphene nanoparticles) hybrid nanocomposite. The obtained results (Fig. 17) revealed an improvement of 19.72% in microhardness and 77.5% of compressive strength in comparison with the base metal (AZ31 Magnesium alloy), processed with a tool rotational speed of 1400 rpm.

In a similar study, the friction and wear performance of AZ31/n-Al₂O₃ - CNT hybrid composites fabricated using FSP method were investigated in comparison with AZ31 matrix alloy and the composites reinforced with only n- Al₂O₃ or CNT particles (Lu *et al.*, 2013). While all the composite formulations developed in this study displayed better wear resistance compared to AZ31 base alloy, the composite containing only n- Al₂O₃ particles exhibited lower wear rate compared to CNT containing composites, although the frictional coefficient of CNT reinforced composites were larger (Fig. 18). In the case of hybrid composites, a hybrid

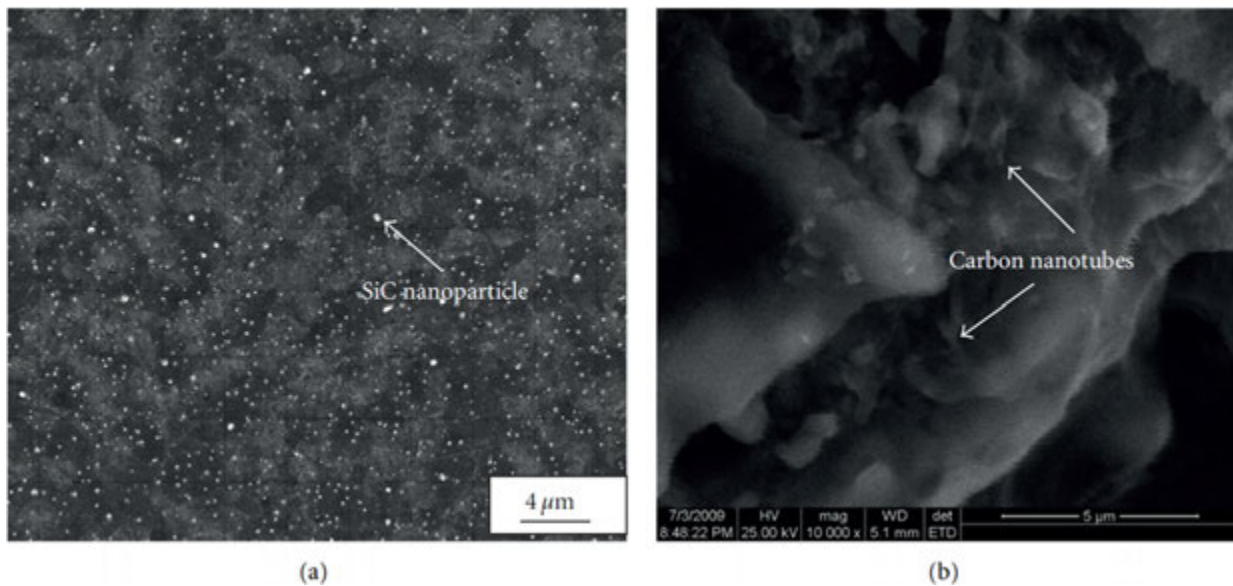


Fig. 14 Distribution of SiC nanoparticles in as-cast AZ91/0.7CNT-0.3SiC. (b) CNTs distributed in the fractograph of the hybrid composites. Reproduced from Zhou, X., *et al.*, 2012. Tensile mechanical properties and strengthening mechanism of hybrid carbon nanotube and silicon carbide nanoparticle-reinforced magnesium alloy composites. *Journal of Nanomaterials* 2012, 851862. Available at: <https://doi.org/10.1155/2012/851862>.

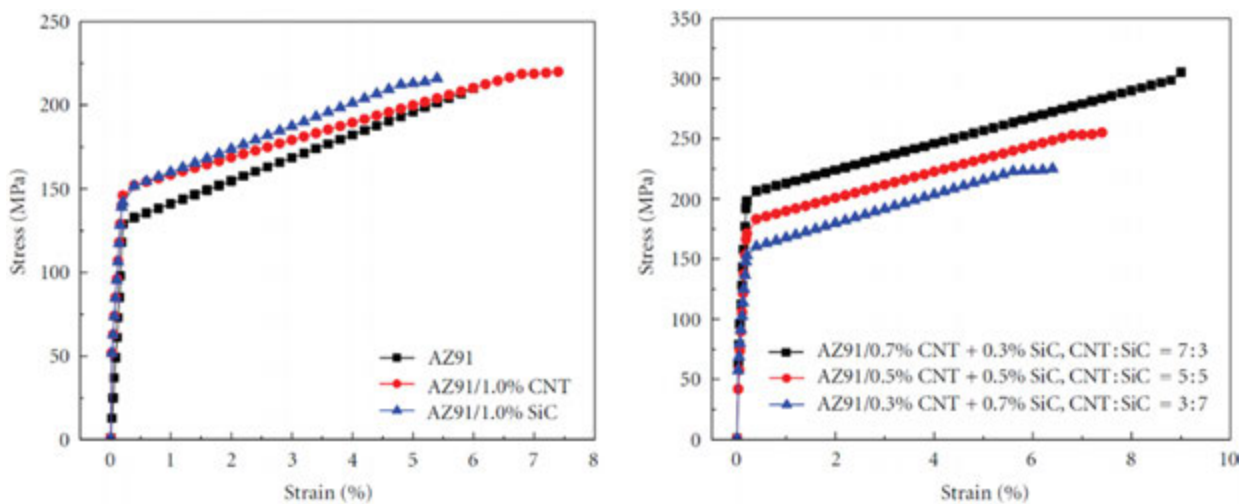


Fig. 15 Tensile properties of AZ91/CNT-SiC hybrid composites. Reproduced from Zhou, X., *et al.*, 2012. Tensile mechanical properties and strengthening mechanism of hybrid carbon nanotube and silicon carbide nanoparticle-reinforced magnesium alloy composites. *Journal of Nanomaterials* 2012, 851862. Available at: <https://doi.org/10.1155/2012/851862>.

effect was reported. For loads larger than 1.95 MPa, the wear of AZ31/0.1Al₂O₃-0.2CNT was considerably lower compared to other composite formulations. Further, it was also reported that the wear mechanism was generally the delamination of mechanically mixed layer at normal loads greater than 1.3 MPa which transforms into abrasive wear when the normal load was lower than 1.3 MPa.

Development of Magnesium Based Composites Using Disintegrated Melt Deposition Followed by Hot Extrusion

Ugandhar *et al.* (Sinha *et al.*, 2006; Ugandhar *et al.*, 2006) used an innovative disintegrated melt deposition (DMD) technique (Fig. 19) to fabricate hybrid Mg composites containing micron sized SiC and Ti particles. The developed composites were investigated for their mechanical and tribological properties in hot-extruded condition. The results of mechanical characterization revealed an increase in the hardness, modulus and yield strength of the composite alongside reduction in the average CTE value (Table 5).

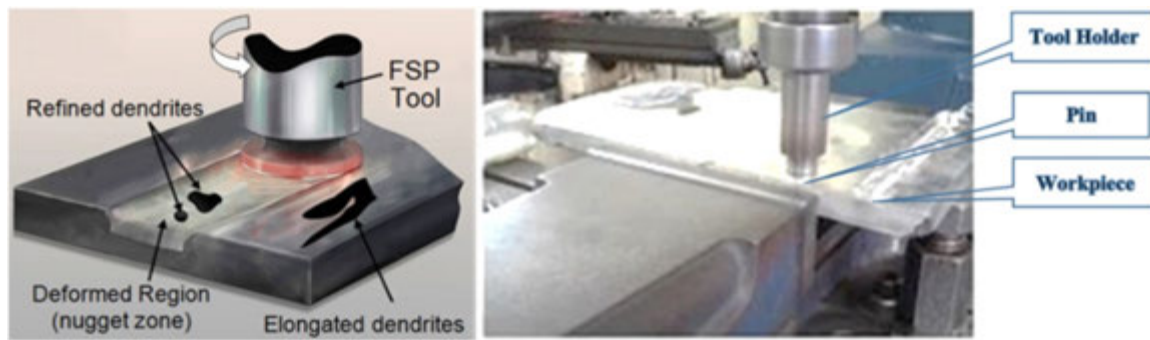


Fig. 16 Schematic illustration of friction stir processing. Reproduced from Arokiasamy, S., Anand Ronald, B., 2017. Experimental investigations on the enhancement of mechanical properties of magnesium-based hybrid metal matrix composites through friction stir processing. *International Journal of Advanced Manufacturing Technology* 93, 493–503. Available at: <https://doi.org/10.1007/s00170-017-0221-5>. Arokiasamy, S., Anand Ronald, B., 2018. Enhanced properties of magnesium based metal matrix composites via Friction Stir Processing 5 (2), 6934–6939. *Materials Today Proceedings*. Available at: <https://doi.org/10.1016/j.matpr.2017.11.355>.

Table 4 FSP parameters and microstructure/hardness testing results from Arokiasamy and Anand Ronald

Sample Code	Rotating Speed RPM	Linear Speed mm/min	Shoulder Dia-meter mm	Pin Dia-meter mm	Aspect Ratio NA	Grain Size μm	Hard-ness Hv	Wear rate cm^3/m
MMC	Not applicable					82	59.3	4.3888
FSP 1	220	10	16.5	5.5	3	22	64.7	6.0588
FSP 2	360	10	16.5	5.5	3	15	67.6	3.0588
FSP 3	540	10	16.5	5.5	3	7	69.7	5.0588
FSP 4	220	20	16.5	5.5	3	14	65.2	8.7058
FSP 5	360	20	16.5	5.5	3	9	68.5	8.8888
FSP 6	540	20	16.5	5.5	3	9	68.5	7.2947

Note: Arokiasamy, S., Anand Ronald, B., 2017. Experimental investigations on the enhancement of mechanical properties of magnesium-based hybrid metal matrix composites through friction stir processing. *International Journal of Advanced Manufacturing Technology* 93, 493–503. Available at: <https://doi.org/10.1007/s00170-017-0221-5>. Arokiasamy, S., Anand Ronald, B., 2018. Enhanced properties of magnesium based metal matrix composites via Friction Stir Processing. *Materials Today Proceedings* 5(2), 6934–6939. Available at: <https://doi.org/10.1016/j.matpr.2017.11.355>.

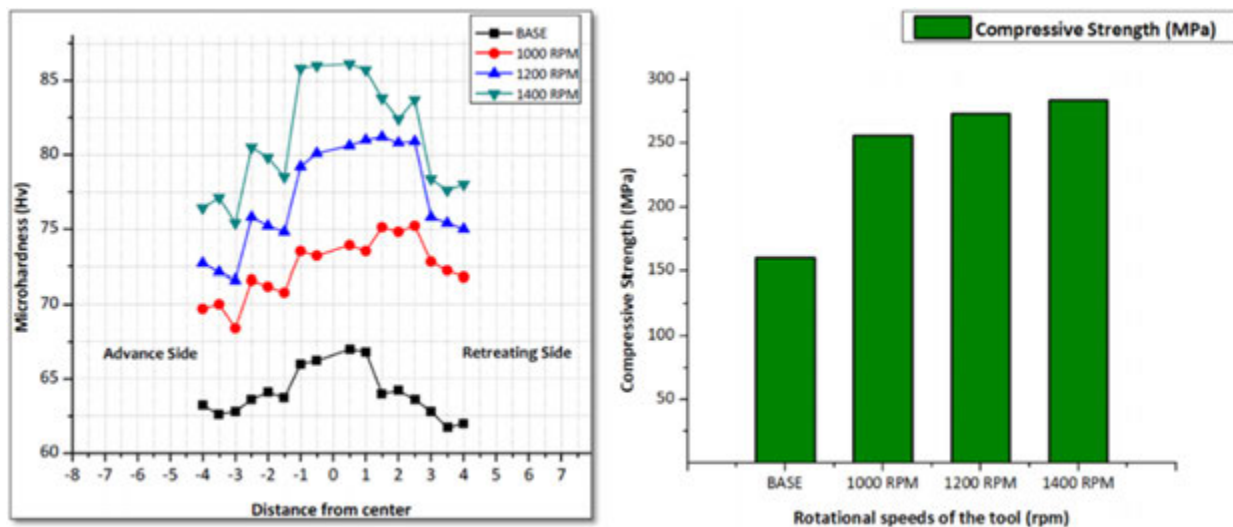
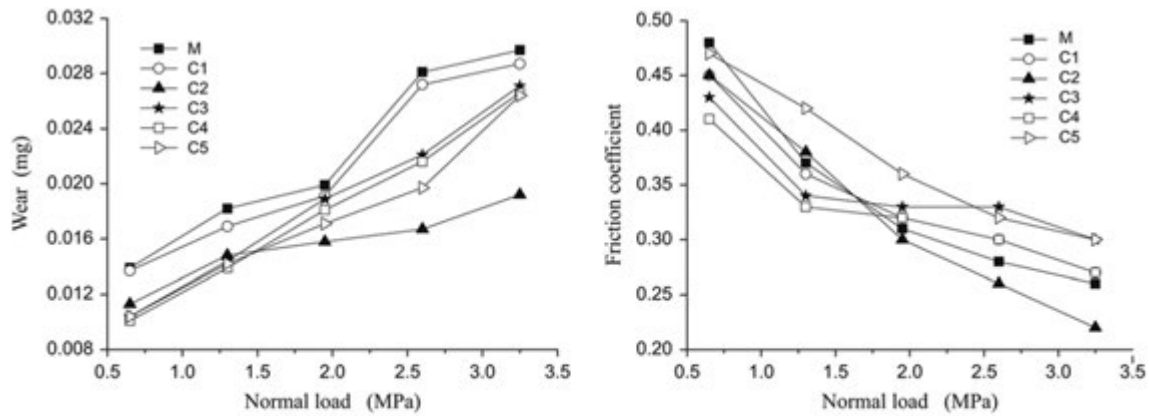


Fig. 17 Microhardness and compressive properties of FSP processed AZ31/CNT-GNP hybrid composites. Reproduced from Sharma, S., et al., 2019. Influence of tool rotation speeds on mechanical and morphological properties of friction stir processed nano hybrid composite of MWCNT-Graphene-AZ31 magnesium. *Journal of Magnesium and Alloys* 7 (3), 487–500. Available at: <https://doi.org/10.1016/j.jma.2019.07.001>.



M: No reinforcement; C1: 0.3% CNTs; C2: 0.1% Al_2O_3 and 0.2% CNTs; C3: 0.15% Al_2O_3 and 0.15% CNTs; C4: 0.2% Al_2O_3 and 0.1% CNTs; C5: 0.3% Al_2O_3

Fig. 18 Wear and friction coefficients of FSP AZ31/CNT- Al_2O_3 hybrid composites. Reproduced from Lu, D., Jiang, Y., Zhou, R., 2013. Wear performance of nano- Al_2O_3 particles and CNTs reinforced magnesium matrix composites by friction stir processing. *Wear* 305 (1-2), 286–290. Available at: <https://doi.org/10.1016/j.wear.2012.11.079>.

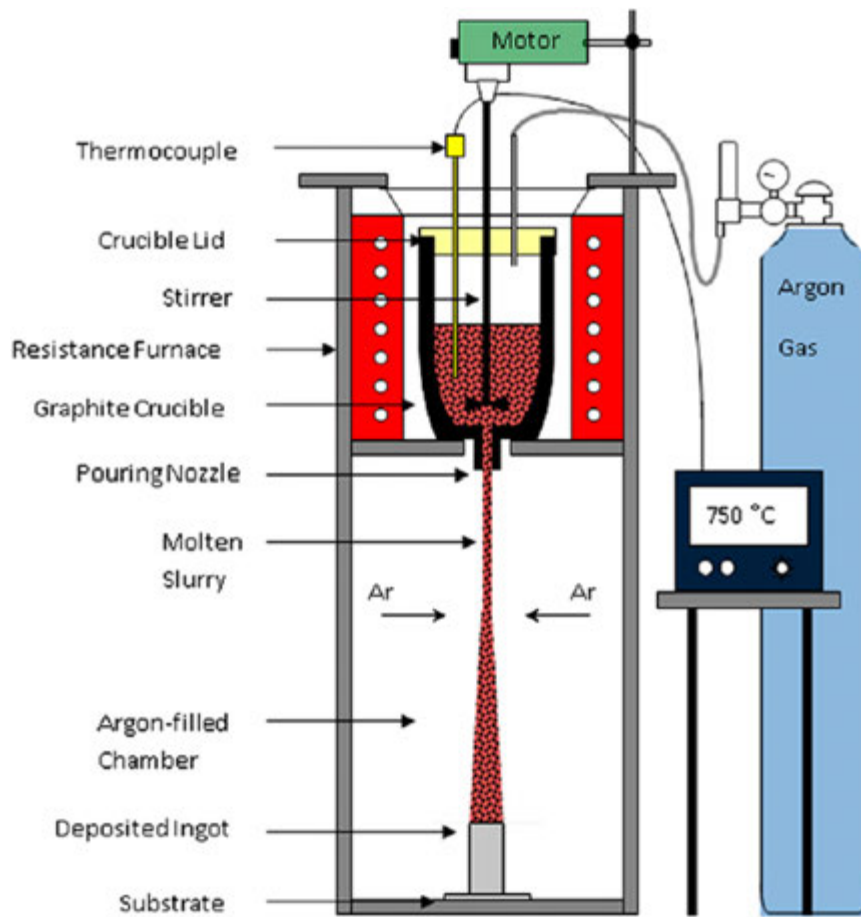


Fig. 19 Schematic illustration of disintegrated melt deposition technique. Reproduced from Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 3–46. Available at: <https://doi.org/10.1016/j.matchar.2015.04.015>.

Table 5 Mechanical properties and Scratch hardness of Mg/SiC-Ti hybrid composites

Materials	Hardness (HR 15T)	Dynamic modulus (GPa)	Yield strength (MPa)	Ultimate tensile strength (MPa)	Ductility (%)	Scratch hardness	
						Normal load (0.55 N)	Normal load (0.75 N)
Mg	47 ± 1	39.82	153 ± 8	207 ± 4	9.2 ± 1.0	721 ± 25	719 ± 22
Mg/4.8SiC	58 ± 1	45.60	182 ± 2	219 ± 2	2.1 ± 0.9	868 ± 38	864 ± 24
Mg/10.25SiC	59 ± 1	47.22	171 ± 3	221 ± 14	1.5 ± 0.2	932 ± 47	929 ± 7
Mg/15.4SiC	63 ± 1	48.24	155 ± 1	207 ± 9	1.4 ± 0.1	973 ± 32	967 ± 33
Mg/5.02SiC-2.7Ti	48 ± 2	46.76	169 ± 9	204 ± 17	2.7 ± 0.7	847 ± 18	840 ± 12
Mg/9.92SiC-2.7Ti	52 ± 1	47.96	161 ± 9	199 ± 16	2.9 ± 1.0	951 ± 68	939 ± 28
Mg/14.93SiC-2.7Ti	65 ± 1	51.81	217 ± 2	233 ± 6	1.0 ± 0.1	969 ± 44	956 ± 21

Note: Sinha, S.K., Reddy, S.U., Gupta, M., 2006. Scratch hardness and mechanical property correlation for Mg/SiC and Mg/SiC/Ti metal-matrix composites. *Tribology International* 39 (2), 184–189. Available at: <https://doi.org/10.1016/j.triboint.2005.04.017>. Ugandhar, S., Gupta, M., Sinha, S.K., 2006. Effect of hybrid metallic and ceramic reinforcements on the properties of pure magnesium. *Solid State Phenomena* 111, 79–82. Available at: <https://doi.org/10.4028/www.scientific.net/SSP.111.79>.

Table 6 Mechanical properties of Mg-based hybrid composites developed by Sankaranarayanan *et al.*

Material	CTE (μK)	Micro-hardness (HV)	Tensile yield strength (MPa)	Ultimate tensile strength (MPa)	Failure strain (%)	Compressive yield strength (MPa)	Ultimate compressive strength (MPa)	Failure strain (%)
Mg	28.52	48 ± 1	125 ± 9	169 ± 11	6.2 ± 0.7	87 ± 4	240 ± 9	19.2 ± 0.7
Mg/Ti	—	71 ± 2	158 ± 6	226 ± 6	8.0 ± 1.5	77 ± 3	347 ± 5	13.5 ± 0.8
Mg/Ti-Al ₂ O ₃	23.73	74 ± 2	175 ± 4	227 ± 10	3.3 ± 0.2	106 ± 0	424 ± 15	14.4 ± 1.2
Mg/(Ti + Al ₂ O ₃) _{BM}	23.53	69 ± 1	168 ± 8	214 ± 8	6.8 ± 0.8	106 ± 3	349 ± 9	15.2 ± 1.7
Mg/Cu	—	82 ± 4	182 ± 4	220 ± 4	8.9 ± 0.9	102 ± 8	386 ± 4	21.1 ± 1.7
Mg/Ti-Cu	—	86 ± 2	196 ± 9	227 ± 4	5.7 ± 1.6	116 ± 5	342 ± 3	16.1 ± 1.4
Mg/(Ti + Cu) _{BM}	—	91 ± 3	201 ± 7	265 ± 11	7.5 ± 0.8	126 ± 8	380 ± 6	19.1 ± 2.9
Mg/Al	—	65 ± 2	161 ± 5	250 ± 0	7.5 ± 1.1	127 ± 2	437 ± 5	21.7 ± 4.3
Mg/Ti-Al	29.05	78 ± 3	167 ± 5	236 ± 5	4.8 ± 0.5	104 ± 1	378 ± 13	12.6 ± 1.3
Mg/(Ti + Al) _{BM}	26.13	93 ± 3	194 ± 2	265 ± 2	4.8 ± 0.6	139 ± 6	431 ± 14	12.9 ± 1.6

Note: Sankaranarayanan, S., Jayalakshmi, S., Gupta, M., 2011a. Effect of addition of mutually soluble and insoluble metallic elements on the microstructure, tensile and compressive properties of pure magnesium. *Materials Science and Engineering A*, 149–160. Available at: <https://doi.org/10.1016/j.msea.2011.09.066>. Sankaranarayanan, S., Jayalakshmi, S., Gupta, M., 2011b. Effect of ball milling the hybrid reinforcements on the microstructure and mechanical properties of Mg-(Ti + n-Al₂O₃) composites. *Journal of Alloys and Compounds* 509 (26), 7229–7237. Available at: <https://doi.org/10.1016/j.jallcom.2011.04.083>. Seetharaman, S., *et al.*, 2012. Influence of micron-Ti and Nano-Cu additions on the microstructure and mechanical properties of pure magnesium. *Metals* 2 (3), 274–291. Available at: <https://doi.org/10.3390/met2030274>.

Table 7 Mechanical properties of Mg/Ti composites containing micro-Ti particles hybridized with nano-SiC or B₄C particles

Materials	Micro-hardness (HV)	Tensile yield strength (MPa)	Ultimate tensile strength (MPa)	Failure strain (%)	Compressive Yield Strength (MPa)	Ultimate Compressive Strength (MPa)	Failure Strain (%)
Pure Mg	48 ± 1	120 ± 9	169 ± 11	6.2 ± 0.7	65 ± 4	248 ± 8	19.2 ± 1.1
Mg/5.6Ti	71 ± 2	158 ± 6	226 ± 6	8.0 ± 1.5	77 ± 3	347 ± 5	13.5 ± 0.8
Mg/(5.6Ti + 0.5B ₄ C) _{BM}	70 ± 4	156 ± 9	228 ± 12	11.7 ± 0.4	77 ± 7	372 ± 3	15.8 ± 0.5
Mg/(5.6Ti + 1.5B ₄ C) _{BM}	87 ± 5	180 ± 5	238 ± 6	9.8 ± 0.7	96 ± 7	395 ± 5	15.6 ± 1.3
Mg/(5.6Ti + 2.5B ₄ C) _{BM}	92 ± 7	215 ± 9	260 ± 8	8.1 ± 0.3	118 ± 5	419 ± 7	13.0 ± 0.5
Mg/(5.6Ti + 0.5SiC) _{BM}	74 ± 4	167 ± 4	228 ± 5	9.6 ± 0.6	101 ± 7	358 ± 9	14.5 ± 1.2
Mg/(5.6Ti + 1.0SiC) _{BM}	83 ± 3	204 ± 7	260 ± 3	9.2 ± 1.1	117 ± 6	391 ± 7	13.1 ± 1.1
Mg/(5.6Ti + 2.0SiC) _{BM}	86 ± 5	192 ± 4	250 ± 3	4.6 ± 0.8	121 ± 6	379 ± 10	10.7 ± 0.9

Note: Sankaranarayanan, S., *et al.*, 2013. Effect of hybridizing micron-sized Ti with nano-sized SiC on the microstructural evolution and mechanical response of Mg-5.6Ti composite. *Journal of Alloys and Compounds* 575, 207–217. Available at: <https://doi.org/10.1016/j.jallcom.2013.04.095>. Sankaranarayanan, S., *et al.*, 2014. Microstructural evolution and mechanical properties of Mg composites containing nano-B₄C hybridized micro-Ti particulates. *Materials Chemistry and Physics* 143 (3), 1178–1190. Available at: <https://doi.org/10.1016/j.matchemphys.2013.11.019>.

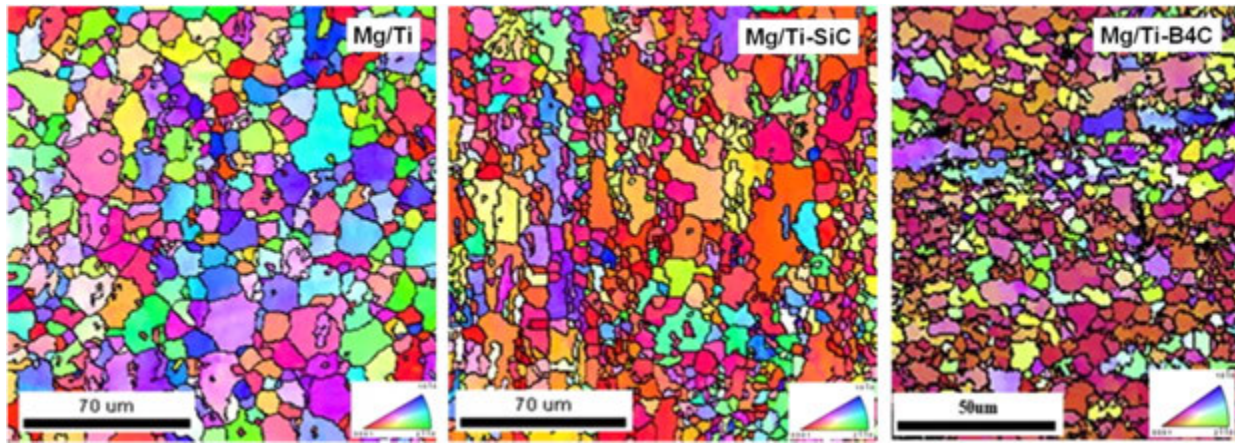


Fig. 20 Microstructure of nanoscale SiC and B4C hybridized Mg/Ti composites and the interfacial characteristics of Mg/(Ti + SiC) hybrid composite. Reproduced from Sankaranarayanan, S., *et al.*, 2013. Effect of hybridizing micron-sized Ti with nano-sized SiC on the microstructural evolution and mechanical response of Mg-5.6Ti composite. *Journal of Alloys and Compounds* 575, 207–217. Available at: <https://doi.org/10.1016/j.jallcom.2013.04.095>. Sankaranarayanan, S., *et al.*, 2014. Microstructural evolution and mechanical properties of Mg composites containing nano-B4C hybridized micro-Ti particulates. *Materials Chemistry and Physics* 143 (3), 1178–1190. Available at: <https://doi.org/10.1016/j.matchemphys.2013.11.019>.

Table 8 Effect of Ni and Cu additions on the mechanical properties of AZ31B/Al₂O₃ nanocomposites

Materials	CTE (μ/K)	Hardness (HV)	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)
AZ31B	26.23	63 $\pm$ 1	201 $\pm$ 7	270 $\pm$ 6	5.6 $\pm$ 1.4
AZ31B/1.5Al ₂ O ₃	24.73	86 $\pm$ 3	144 $\pm$ 9	214 $\pm$ 16	29.5 $\pm$ 1.9
AZ31B/1.5 Al ₂ O ₃ –1.5Ni	22.75	93 $\pm$ 4	227 $\pm$ 4	298 $\pm$ 5	5.7 $\pm$ 0.7
AZ31B/1.5 Al ₂ O ₃ –3.19Ni	21.34	102 $\pm$ 4	251 $\pm$ 8	306 $\pm$ 6	2.5 $\pm$ 0.4
AZ31B/2Cu	25.34	95 $\pm$ 3	238 $\pm$ 8	298 $\pm$ 6	4.5 $\pm$ 0.5
AZ31B/1.5 Al ₂ O ₃ –2Cu	23.08	103 $\pm$ 3	250 $\pm$ 11	301 $\pm$ 11	13.5 $\pm$ 2.1
AZ31B/4Cu	23.86	105 $\pm$ 3	265 $\pm$ 8	308 $\pm$ 9	1.9 $\pm$ 0.4
AZ31B/1.5 Al ₂ O ₃ –4Cu	22.15	112 $\pm$ 2	300 $\pm$ 12	350 $\pm$ 14	8.5 $\pm$ 1.6

Note: Nguyen, Q.B., *et al.*, 2011. Enhancing strength and hardness of AZ31B through simultaneous addition of nickel and nano-Al₂O₃ particulates. *Materials Science and Engineering A* 528 (3), 888–894. Available at: <https://doi.org/10.1016/j.msea.2010.10.021>. Nguyen, Q.B., *et al.*, 2012a. Simultaneous effect of nano-Al₂O₃ and micrometre Cu particulates on microstructure and mechanical properties of magnesium alloy AZ31. *Materials Science and Technology* 28 (2), 227–233. Available at: <https://doi.org/10.1179/1743284711Y.0000000023>.

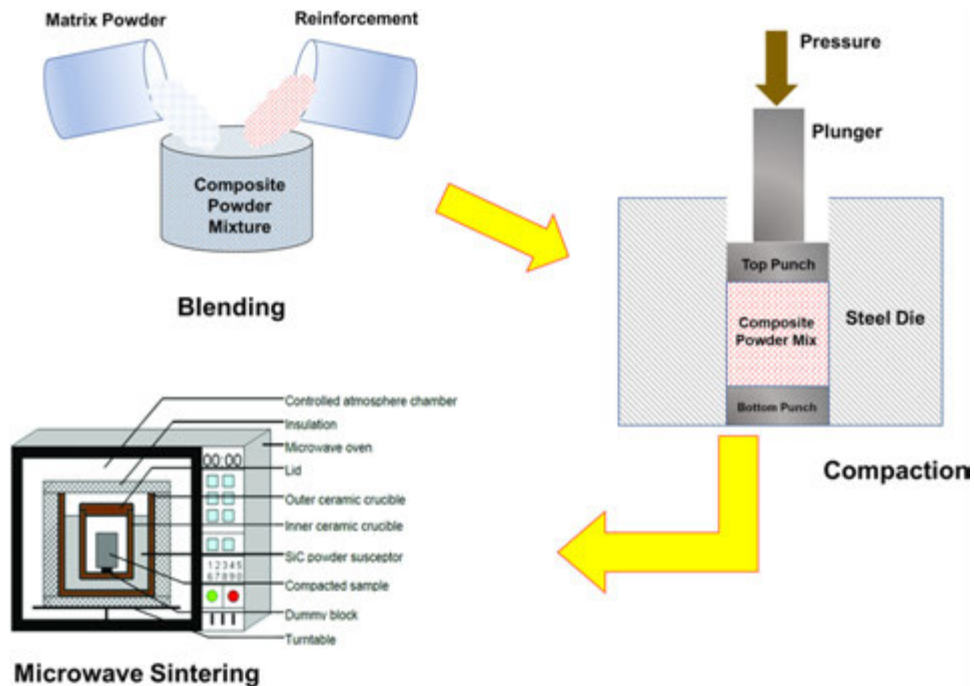


Fig. 21 Schematic illustration of microwave rapid sintering assisted powder metallurgy technique.

Table 9 Mechanical properties of Mg/SiC-Al₂O₃ and Mg/SiC-CNT hybrid composites developed by Thakur *et al.*

Materials	Micro-hardness (Hv)	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)
Mg	41 ± 1	111.9 ± 7.7	155.8 ± 2.1	5.9 ± 1.2
Mg/0.7SiC-0.3CNT	46 ± 1	152.9 ± 4.1	195.4 ± 4.7	3.3 ± 0.7
Mg/0.5SiC-0.5CNT	45 ± 1	152.1 ± 1.2	188.5 ± 2.7	2.3 ± 0.6
Mg/0.5SiC-0.5Al ₂ O ₃	46 ± 1	155.7 ± 7.0	197.4 ± 1.8	4.6 ± 2.1
Mg/0.3SiC-0.7Al ₂ O ₃	48 ± 1	164.9 ± 1.4	206.1 ± 5.3	4.2 ± 1.8
Mg/0.3SiC-0.7CNT	44 ± 1	139.5 ± 6.5	182.9 ± 7.5	2.1 ± 0.5
Mg/1SiC	43 ± 1	117.0 ± 6.2	153.8 ± 2.8	1.5 ± 0.3

Note: Thakur, S.K., Balasubramanian, K., Gupta, M., 2007a. Microwave synthesis and characterization of magnesium based composites containing nanosized SiC and hybrid (SiC + Al₂O₃) reinforcements. *Journal of Engineering Materials and Technology*, Transactions of the ASME 129 (2), 194–199. Available at: <https://doi.org/10.1115/1.2400279>. Thakur, S. K., Kwee, G.T., Gupta, M., 2007b. Development and characterization of magnesium composites containing nano-sized silicon carbide and carbon nanotubes as hybrid reinforcements. *Journal of Materials Science* 46 (15), 1879–1887. Available at: <https://doi.org/10.1007/s10853-007-2004-0>.

Table 10 Mechanical properties of Mg hybrid composites developed by Tun *et al.*

Materials	Micro-hardness (Hv)	Tensile properties			Compressive properties		
		Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)
Mg	37 ± 2	134 ± 7	193 ± 1	6.9 ± 2.5	70 ± 7	280 ± 9	28.1 ± 2.9
Mg/0.7Y ₂ O ₃	45 ± 2	157 ± 10	244 ± 1	9.1 ± 0.6	–	–	–
Mg/0.7 Y ₂ O ₃ –0.3Ni	54 ± 4	221 ± 7	262 ± 6	9.0 ± 0.9	154 ± 5	402 ± 3	17.2 ± 0.2
Mg/0.7 Y ₂ O ₃ –0.6Ni	60 ± 4	232 ± 8	272 ± 2	9.5 ± 0.9	154 ± 9	394 ± 4	16.3 ± 0.4
Mg/0.7 Y ₂ O ₃ –1.0Ni	63 ± 4	228 ± 8	271 ± 6	5.5 ± 0.7	154 ± 9	406 ± 8	16.0 ± 0.4
Mg	40 ± 0	126 ± 3	200 ± 9	10.3 ± 2.9	66 ± 4	186 ± 2	22 ± 1
Mg/1.5Ni	54 ± 1	127 ± 2	242 ± 10	7.6 ± 0.8	120 ± 13	228 ± 12	18 ± 3
Mg/0.33TiO ₂	37 ± 0	116 ± 14	202 ± 6	12.1 ± 1.2	754 ± 4	201 ± 4	23 ± 4
Mg/0.66 TiO ₂	39 ± 1	113 ± 13	197 ± 6	11.5 ± 3.2	92 ± 5	249 ± 6	20 ± 2
Mg/1.00 TiO ₂	40 ± 1	113 ± 5	190 ± 9	11.8 ± 1.6	109 ± 4	256 ± 4	23 ± 1
Mg/1.50Ni-0.33 TiO ₂	60 ± 1	144 ± 8	249 ± 11	11.9 ± 1.0	140 ± 11	240 ± 10	19 ± 1
Mg	42 ± 2	111 ± 8	177 ± 10	9.8 ± 2.2	109 ± 4	284 ± 11	23 ± 3
Mg/0.3ZrO ₂	40 ± 1	84.8 ± 8	139 ± 8	8.1 ± 1.6	109 ± 6	273 ± 13	19 ± 1
Mg/0.6 ZrO ₂	42 ± 2	117 ± 11	182 ± 14	9.4 ± 2.7	–	–	–
Mg/1.0 ZrO ₂	42 ± 2	98 ± 6	158 ± 12	8.6 ± 2.2	109 ± 5	262 ± 18	19 ± 4
Mg/1.0 ZrO ₂	40 ± 1	122 ± 8	188 ± 6	10.0 ± 1.3	–	–	–
Mg/0.3 ZrO ₂ –0.7Cu	48 ± 1	196 ± 16	249 ± 8	8.2 ± 1.1	124 ± 7	352 ± 18	12 ± 3
Mg/0.6 ZrO ₂ –0.4Cu	50 ± 1	139 ± 22	193 ± 21	11.4 ± 2.9	–	–	–
Mg	40 ± 1	121 ± 5	179 ± 6	11.4 ± 1.1	103 ± 4	263 ± 5	22 ± 2
Mg/1Al ₂ O ₃ –0.1Cu	49 ± 2	169 ± 11	205 ± 11	2.8 ± 0.4	115 ± 4	265 ± 13	10 ± 1
Mg/1 Al ₂ O ₃ –0.3Cu	56 ± 2	190 ± 13	225 ± 13	4.1 ± 0.6	119 ± 8	349 ± 7	10 ± 4
Mg/1 Al ₂ O ₃ –0.6Cu	68 ± 2	184 ± 7	224 ± 8	9.5 ± 1.2	136 ± 8	397 ± 7	13 ± 1
Mg/1 Al ₂ O ₃ –0.9Cu	59 ± 2	202 ± 7	232 ± 7	4.1 ± 0.3	156 ± 13	368 ± 7	9 ± 4

Note: Tun, K.S., Gupta, M., 2009. Development of magnesium/(yttria + nickel) hybrid nanocomposites using hybrid microwave sintering: Microstructure and tensile properties. *Journal of Alloys and Compounds* 487 (1–2), 76–82. Available at: <https://doi.org/10.1016/j.jallcom.2009.07.117>. Tun, K.S., Gupta, M., 2010a. Compressive deformation behavior of Mg and Mg/(Y₂O₃ + Ni) nanocomposites. *Materials Science and Engineering A* 527 (21–22), 5550–5556. Available at: <https://doi.org/10.1016/j.msea.2010.05.025>. Tun, K.S., Gupta, M., 2010b. Role of microstructure and texture on compressive strength improvement of Mg/(Y₂O₃ + Cu) hybrid nanocomposites. *Journal of Composite Materials* 44 (25), 3033–3050. Available at: <https://doi.org/10.1177/0021998310369591>. Tun, K.S., *et al.*, 2012. Enhancing tensile and compressive strengths of magnesium using nanosize (Al₂O₃ + Cu) hybrid reinforcements. *Journal of Composite Materials* 46 (15), 1879–1887. Available at: <https://doi.org/10.1177/0021998311427767>. Tun, K.S., *et al.*, 2013. Tensile and compressive responses of ceramic and metallic nanoparticle reinforced Mg composites. *Materials* 6(5), 1826–1839. Available at: <https://doi.org/10.3390/ma6051826>. Fida Hassan, S., *et al.*, 2015a. Effect of copper nano particles on high temperature tensile behavior of Mg-Y₂O₃ nanocomposite. *Metals and Materials International*. (3), Available at: <https://doi.org/10.1007/s12540-015-4188-1>. Fida Hassan, S., *et al.*, 2016. Magnesium nanocomposite: increasing copperisation effect on high temperature tensile properties. *Powder Metallurgy* Available at: <https://doi.org/10.1080/00325899.2015.1109816>. Hassan, S.F., *et al.*, 2016. Microwave sintered magnesium nanocomposite: Hybrid (Y₂O₃ + Ni) nano-size reinforcement and ensile properties. *Advanced Composites Letters* 25 (4), 103–107. Available at: <https://doi.org/10.1177/096369351602500404>. Olalekan, O., 2016. Development of Magnesium Based Hybrid Nanocomposite. King Fahd University of Petroleum and Minerals, Saudi Arabia. Available at: <http://search.proquest.com/openview/507fd960dc966269fb6dbe8c917a1b4d/1?pq-origsite=gscholar&cbl=2026366&diss=y>.

However, the ductility was adversely affected. Further, the results of scratch hardness tests also correlated well with the hardness and elastic hardness i.e. increase with an increase in the weight percent of the reinforcing particulates (Table 5).

The properties of DMD processed Mg/Ti based hybrid composites reinforced with nanoscale Al₂O₃ or Cu particles were also investigated (Sankaranarayanan *et al.*, 2011b; Seetharaman *et al.*, 2012). In this study, the hybrid reinforcement mixture was pre-

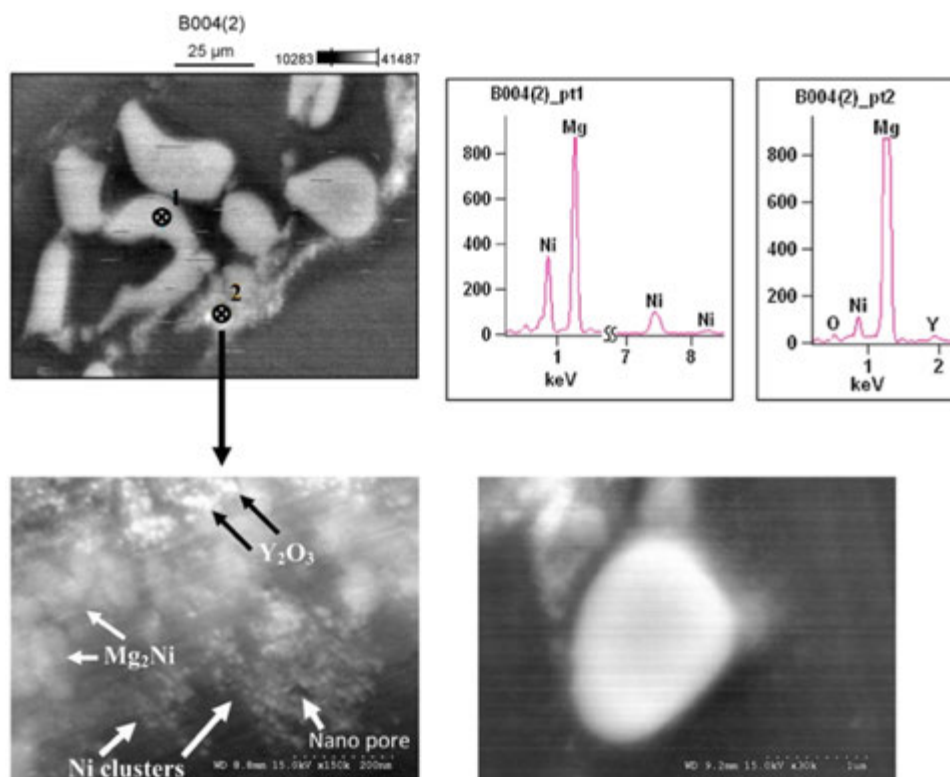


Fig. 22 Micrographs showing the presence of nickel, yttria and Mg_2Ni intermetallics in Mg matrix. Reproduced from Tun, K.S., Gupta, M., 2009. Development of magnesium/(yttria + nickel) hybrid nanocomposites using hybrid microwave sintering: Microstructure and tensile properties. *Journal of Alloys and Compounds* 487 (1-2), 76–82. Available at: <https://doi.org/10.1016/j.jallcom.2009.07.117>.

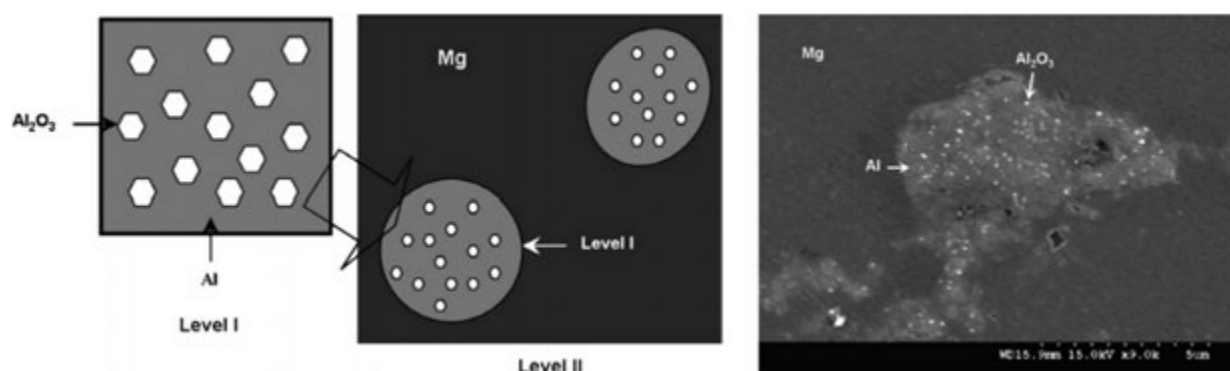


Fig. 23 Schematic of the hierarchical Mg composites synthesized by Habibi *et al.* Reproduced from Habibi, M.K., Joshi, S.P., Gupta, M., 2010. Hierarchical magnesium nano-composites for enhanced mechanical response. *Acta Materialia* 58 (18), 6104–6114. Available at: <https://doi.org/10.1016/j.actamat.2010.07.028>.

processed using the solid-state processing technique of ball-milling with an aim of understanding the influence of hybrid reinforcement pre-processing on the microstructure and mechanical properties of bulk Mg hybrid composites. While the microstructural and mechanical analyses showed significant grain refinement and strength properties enhancement due to hybrid reinforcement addition either pre-processed or added directly, the strength enhancement occurred at the expense of ductility when the hybrid reinforcements are added directly (Table 6). On the other hand, the addition of pre-processed hybrid reinforcements resulted in similar/increased ductility. The authors (Sankaranarayanan *et al.*, 2011a) also performed the addition of ball-milled (Ti + Al) composite mixture to DMD processed pure Mg to develop Mg/Ti- Al_3Ti composite with better strength properties. In this study, the direction addition of Al and Ti to Mg resulted in Mg/Ti- $Mg_{17}Al_{12}$ composite with relatively lesser strength and ductility. In all the cases, the difference in properties were primarily attributed to the changes in reinforcement morphology due to ball-milling.

Table 11 Tensile and compressive properties of Hierarchical Mg composites reported by Habibi *et al.*

Materials	Tensile properties			Compressive properties		
	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)
Mg	93 ± 1	153 ± 7	7.9 ± 3.4	91 ± 3	235 ± 15	20.3 ± 1.8
Mg/0.647Al-0.66Al ₂ O ₃	164 ± 18	254 ± 23	9.5 ± 1.6	–	–	–
Mg/0.972Al-0.66 Al ₂ O ₃	182 ± 10	276 ± 8	11.2 ± 1.5	164 ± 10	429 ± 11	10.2 ± 1.4
Mg/1.298Al-0.66 Al ₂ O ₃	159 ± 11	255 ± 15	7.1 ± 0.6	–	–	–
Mg/1.950Al-0.66 Al ₂ O ₃	148 ± 10	2733 ±	6.1 ± 1.2	–	–	–
Mg/1Al-0.09CNT	148 ± 2	206 ± 4	9.1 ± 0.6	135 ± 4	337 ± 14	10.1 ± 1.5
Mg/0.5Al-0.18CNT	116 ± 11	186 ± 12	10.9 ± 3.5	–	–	–
Mg/1Al-0.18CNT	128 ± 12	208 ± 8	11.2 ± 2.9	126 ± 5	421 ± 13	12.5 ± 0.4
Mg/1.5Al-0.18CNT	156 ± 13	2223 ± 12	7 ± 0.5	–	–	–
Mg/1Al-0.30CNT	160 ± 08	227 ± 14	8.6 ± 0.4	148 ± 5	424 ± 12	12.4 ± 1.7
Mg/1Al-0.50CNT	168 ± 2	220 ± 6	4.6 ± 0.5	144 ± 10	401 ± 15	10.9 ± 1.5
Mg/0.22B ₄ C	110 ± 15	159 ± 14	9.9 ± 0.6	97 ± 4	337 ± 14	10.0 ± 1.6
Mg/0.66B ₄ C	120 ± 5	164 ± 6	10 ± 0.3	100 ± 5	335 ± 11	11.8 ± 1.8
Mg/1.11B ₄ C	82 ± 11	119 ± 17	5.5 ± 1.2	105 ± 3	331 ± 10	13.3 ± 1.4
Mg/0.92Al-0.66B ₄ C	130 ± 9	238 ± 15	7 ± 0.9	129 ± 5	356 ± 33	9.8 ± 1.5
Mg/0.22Bi ₂ O ₃	135 ± 12	207 ± 13	7.5 ± 0.3	101 ± 9	341 ± 8	13.9 ± 0.7
Mg/0.66 Bi ₂ O ₃	135 ± 13	201 ± 15	6.0 ± 0.5	102 ± 11	387 ± 17	12.0 ± 1.5
Mg/1.11 Bi ₂ O ₃	139 ± 13	205 ± 18	4.9 ± 0.6	108 ± 3	411 ± 6	13.6 ± 1.4
Mg/0.92Al-0.22 Bi ₂ O ₃	172 ± 9	250 ± 6	10.0 ± 1.0	140 ± 18	446 ± 10	13.1 ± 1.5
Mg/0.92Al-0.66 Bi ₂ O ₃	158 ± 13	226 ± 9	6.2 ± 0.7	143 ± 13	430 ± 20	9.0 ± 2.0
Mg/0.92Al-1.11 Bi ₂ O ₃	154 ± 9	216 ± 11	6.1 ± 0.5	115 ± 6	420 ± 15	8.6 ± 3.0

Note: Habibi, M.K., *et al.* 2010. Tensile strength and ductility improvement of magnesium by using ball milled Al-CNT particles as reinforcement. In: Proceedings of the Materials Science and Technology Conference and Exhibition. MS and T'10. Habibi, M.K., *et al.*, 2011. Using integrated hybrid (Al + CNT) reinforcement to simultaneously enhance strength and ductility of magnesium. Composites Science and Technology 71 (5), 734–741. Available at: <https://doi.org/10.1016/j.compscitech.2011.01.021>. Habibi, M.K., *et al.*, 2012a. Differentiating the mechanical response of hierarchical magnesium nano-composites as a function of temperature. Materials and Design 42, 102–110. Available at: <https://doi.org/10.1016/j.matdes.2012.05.037>. Habibi, M.K., Joshi, S.P., Gupta, M., 2010. Hierarchical magnesium nano-composites for enhanced mechanical response. Acta Materialia Available at: <https://doi.org/10.1016/j.actamat.2010.07.028>. Habibi, M.K., Joshi, S.P., Gupta, M., 2011. Development of hierarchical magnesium composites using hybrid microwave sintering. Journal of Microwave Power and Electromagnetic Energy 45 (3), 112–120. Available at: <https://doi.org/10.1080/08327823.2011.11689805>. Habibi, M.K., Hamouda, A.M.S., Gupta, M., 2012b. Enhancing tensile and compressive strength of magnesium using ball milled Al + CNT reinforcement. Composites Science and Technology 72 (2), 290–298. Available at: <https://doi.org/10.1016/j.compscitech.2011.11.015>. Habibi, M.K., Hamouda, A.S., Gupta, M., 2013a. Hybridizing boron carbide (B₄C) particles with aluminum (Al) to enhance the mechanical response of magnesium based nano-composites. Journal of Alloys and Compounds 550, 83–93. Available at: <https://doi.org/10.1016/j.jallcom.2012.09.128>. Habibi, M.K., Hamouda, A. S., Gupta, M., 2013b. Using hierarchical composite approach to improve mechanical response of Mg and Mg-Bi₂O₃ nano-composites. Materials and Design 49, 627–637. Available at: <https://doi.org/10.1016/j.matdes.2013.02.028>.

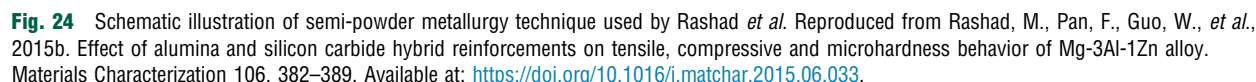
Similar improvements in mechanical properties of Mg/Ti composites were also reported when the Ti particles were hybridized with other nanoscale ceramic and metallic particles such as SiC, B₄C were added (Sankaranarayanan *et al.*, 2013, 2014) (Table 7). Further, the microstructural characterization using EBSD analysis also confirmed more localized recrystallized grains and realignment of basal planes i.e. weak basal fiber texture in the hybrid composites when compared to Mg/Ti (Fig. 20).

Nguyen *et al.* (2011) investigated the effects of Ni particle addition on the performance of AZ31B/1.5 Al₂O₃ nano-composite developed using the method of disintegrated melt deposition (DMD) followed by hot extrusion. It was reported in this study that the addition of 1.5% Ni improved the strength and hardness without significantly affecting the ductility (Table 8). However, the ductility was compromised for AZ31B/1.5 Al₂O₃–3.19Ni. Similar improvement in hardness and strengths were also reported when Cu particles were added to AZ31B/1.5 Al₂O₃ (Nguyen and Gupta, 2010; Nguyen *et al.*, 2012a,b; Nguyen *et al.*, 2012b).

Powder Metallurgy Processing of Magnesium Based Composites Containing Hybrid Reinforcements

Thakur *et al.* (2007a,b) used the microwave assisted powder metallurgy method to develop Mg based hybrid composites. The schematic illustration of the process is shown in Fig. 21. In these studies, the addition of nanoscale reinforcements such as Al₂O₃ and CNT were found to improve the thermal stability and strength properties of Mg/SiC nanocomposites at the expense of ductility (Table 9).

Tun and co-workers (Tun and Gupta, 2009, 2010a,b; Tun *et al.*, 2012, 2013; Fida Hassan *et al.*, 2015a; Fida Hassan *et al.*, 2016; Hassan *et al.*, 2016) also investigated the effects of nanoscale metallic particles addition on the mechanical properties of Mg/Y₂O₃



Materials	Tensile properties			Compressive properties		
	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)
Mg-3Al-1Zn	166 ± 3.8	269 ± 3.1	16.9 ± 1.6	144 ± 3.6	374 ± 5.7	12.92 ± 1.6
After HT	175 ± 2.8	282 ± 3.8	17.42 ± 1.2	–	–	–
Mg-3Al-1Zn/1.5Al ₂ O ₃ -0.2SiC	198 ± 4.1	293 ± 5.0	10.58 ± 2.0	178 ± 5.1	315 ± 4.4	8.44 ± 2.0
After HT	174 ± 3.0	275 ± 5.9	16.5 ± 1.8	–	–	–
Mg-3Al-1Zn/1.5 Al ₂ O ₃ -0.5SiC	208 ± 3.8	306 ± 3.8	7.54 ± 1.8	206 ± 4.2	345 ± 5.0	8.47 ± 1.3
After HT	188 ± 2.6	305 ± 5.3	13.51 ± 2.0	–	–	–
Mg-3Al-1Zn/1.5 Al ₂ O ₃ -1.0SiC	230 ± 2.5	322 ± 2.5	4.32 ± 1.3	238 ± 2.5	402 ± 2.6	7.67 ± 1.1
After HT	196 ± 5.7	311 ± 4.8	14.75 ± 2.1	–	–	–
Pure Mg	104 ± 4	164 ± 5	6.2 ± 1.8	123 ± 5	264 ± 6	9 ± 2.5
Mg-1Cu-0.18GNPs	160 ± 6	240 ± 2	10.4 ± 2.1	140 ± 4	335 ± 8	10.3 ± 1.6
Mg-1Cu-0.36GNPs	184 ± 3	252 ± 3	12.2 ± 1.3	143 ± 6	338 ± 5	11.7 ± 2
Mg-1Cu-0.54GNPs	226 ± 5	260 ± 5	4.8 ± 2.5	166 ± 3	420 ± 6	14.5 ± 1.4
Mg-10Ti	147	212	11.1	–	–	–
Mg-10Ti-1Al	163	238	21.2	–	–	–

Note: Rashad, M., *et al.*, 2015c. Improved mechanical properties of magnesium-graphene composites with copper-graphene hybrids. *Materials Science and Technology* 31 (12). Available at: <https://doi.org/10.1179/1743284714Y.0000000726>. Rashad, M., Pan, F., Asif, M., *et al.*, 2015a. Improved mechanical properties of "magnesium based composites" with titanium-aluminum hybrids. *Journal of Magnesium and Alloys* 3 (1), 1–9. Available at: <https://doi.org/10.1016/j.jma.2014.12.010>. Rashad, M., Pan, F., Guo, W., *et al.*, 2015b. Effect of alumina and silicon carbide hybrid reinforcements on tensile, compressive and microhardness behavior of Mg-3Al-1Zn alloy. *Materials Characterization* 106, 382–389. Available at: <https://doi.org/10.1016/j.matchar.2015.06.033>.

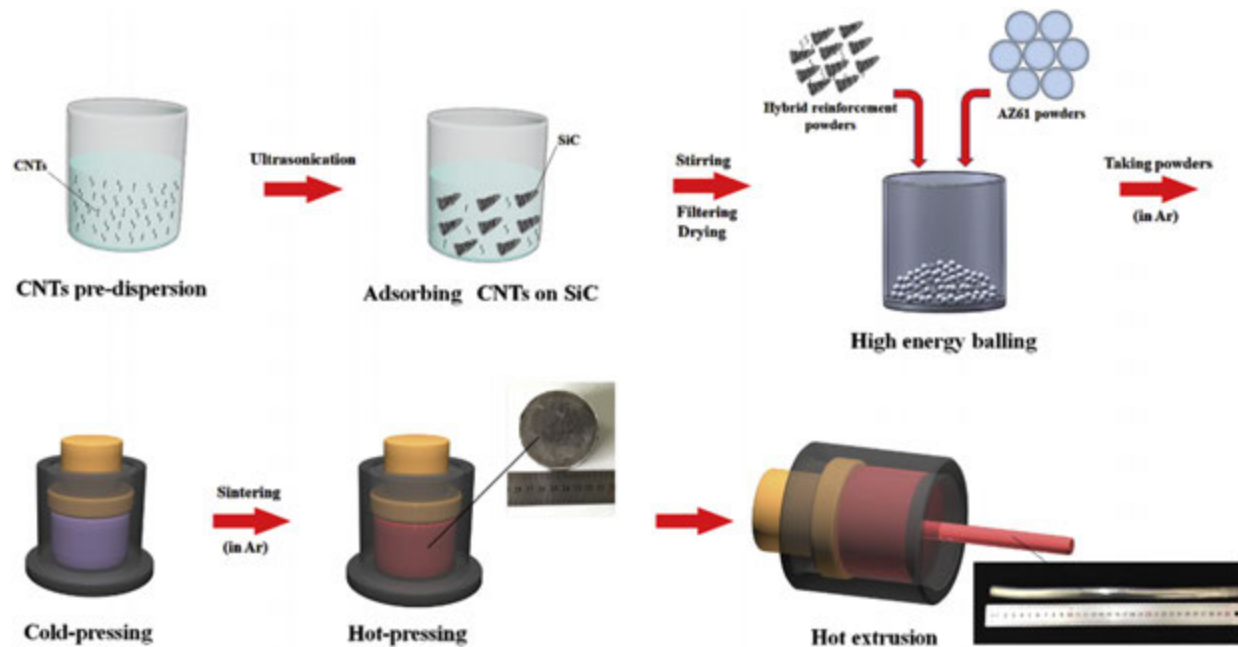


Fig. 25 Schematic illustration of Powder Metallurgy Method used by Zhou *et al.* Reproduced from Zhou, M.Y., *et al.*, 2019b. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. Materials Science and Engineering: A 768, 138447. Available at: <https://doi.org/10.1016/j.msea.2019.138447>.

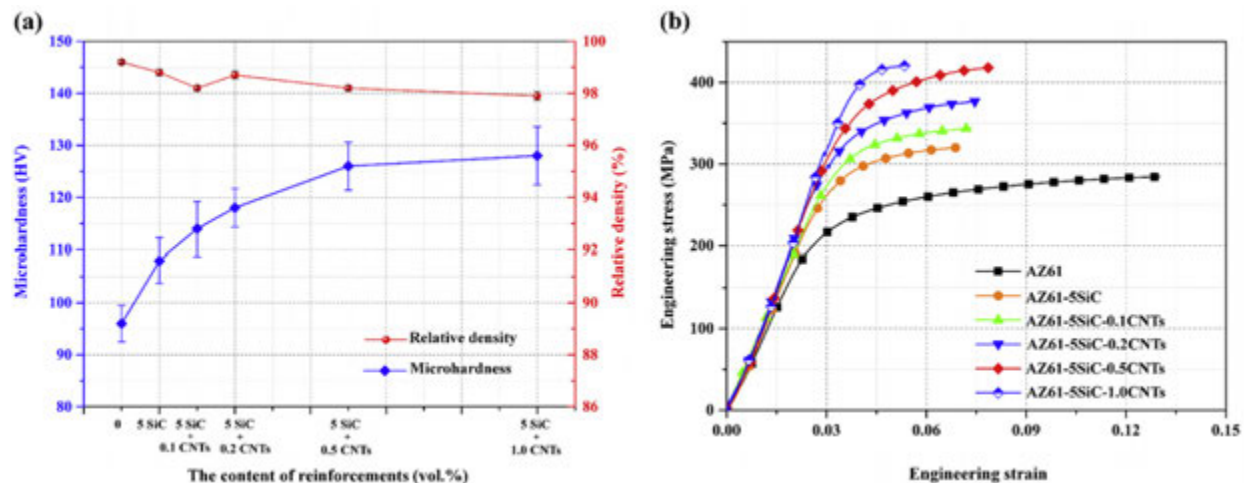


Fig. 26 Mechanical properties of AZ61/SiC-CNT hybrid composites developed by Zhou *et al.* Reproduced from Zhou, M.Y., *et al.*, 2019b. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. Materials Science and Engineering A 768, 138447. Available at: <https://doi.org/10.1016/j.msea.2019.138447>.

nanocomposites. The addition of 0.3–1.0 vol% Ni nanoparticles resulted in remarkable increment in the strength properties and tensile ductility due to combined presence of nanosized Y_2O_3 and Mg_2Ni particles (Table 10, Fig. 22). However, the compressive failure strain was adversely affected due to basal plane realignment causing a steep increment in the work hardening attributes and limited failure strain (Tun and Gupta, 2009, 2010a). Recently, the simultaneous addition of Ni and TiO_2 particles was also reported to improve the hardness, tensile and compressive properties of Mg (Olalekan, 2016). Similar results were also reported for nanoscale copper added to Mg/ Al_2O_3 (Tun *et al.*, 2012), Mg/ Y_2O_3 (Tun and Gupta, 2010b; Fida Hassan *et al.*, 2015a; 2016) and Mg/ ZrO_2 (Tun *et al.*, 2013) nanocomposites.

Recently, Habibi *et al.* (Habibi *et al.*, 2010, 2011, 2012a; Habibi *et al.*, 2010, 2011; Habibi *et al.*, 2012b, 2013a,b) also developed Mg based hybrid composites with hierarchical microstructure configurations (i.e., a composite structure within a composite). In these studies, the powders of Al based nanocomposites containing sub-micron or nanosized particulate reinforcements such as Al_2O_3 , Bi_2O_3 , B_4C and CNT were prepared by ball-milling and the composite powder mixture was then used to

Table 13 Mechanical properties of Mg/SiC-CNT composites reported by Zhou *et al.*

Materials	Grain size (μm)	Microhardness (HV)	Tensile yield strength (MPa)	Ultimate tensile strength (MPa)	Ductility (%)
AZ61	36.4 ± 5.1	96 ± 3.5	208 ± 3.5	285 ± 4.3	13.2 ± 0.4
AZ61/0.5SiC	27.5 ± 3.8	108 ± 4.3	235 ± 4.2	318 ± 5.5	7.0 ± 0.2
AZ61/5SiC-0.1CNT	18.7 ± 5.2	114 ± 5.2	262 ± 3.7	345 ± 3.2	7.4 ± 0.4
AZ61/5SiC-0.2CNT	15.9 ± 4.4	118 ± 3.7	292 ± 4.1	376 ± 3.9	7.6 ± 0.5
AZ61/5SiC-0.5CNT	14.0 ± 3.6	126 ± 4.6	345 ± 4.6	412 ± 5.1	8 ± 0.3
AZ61/5SiC-1.0CNT	13.5 ± 3.8	128 ± 5.6	368 ± 5.5	420 ± 4.0	4.7 ± 0.6

Note: Zhou, M.Y., *et al.*, 2019b. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. Materials Science and Engineering A 768, 138447. Available at: <https://doi.org/10.1016/j.msea.2019.138447>.

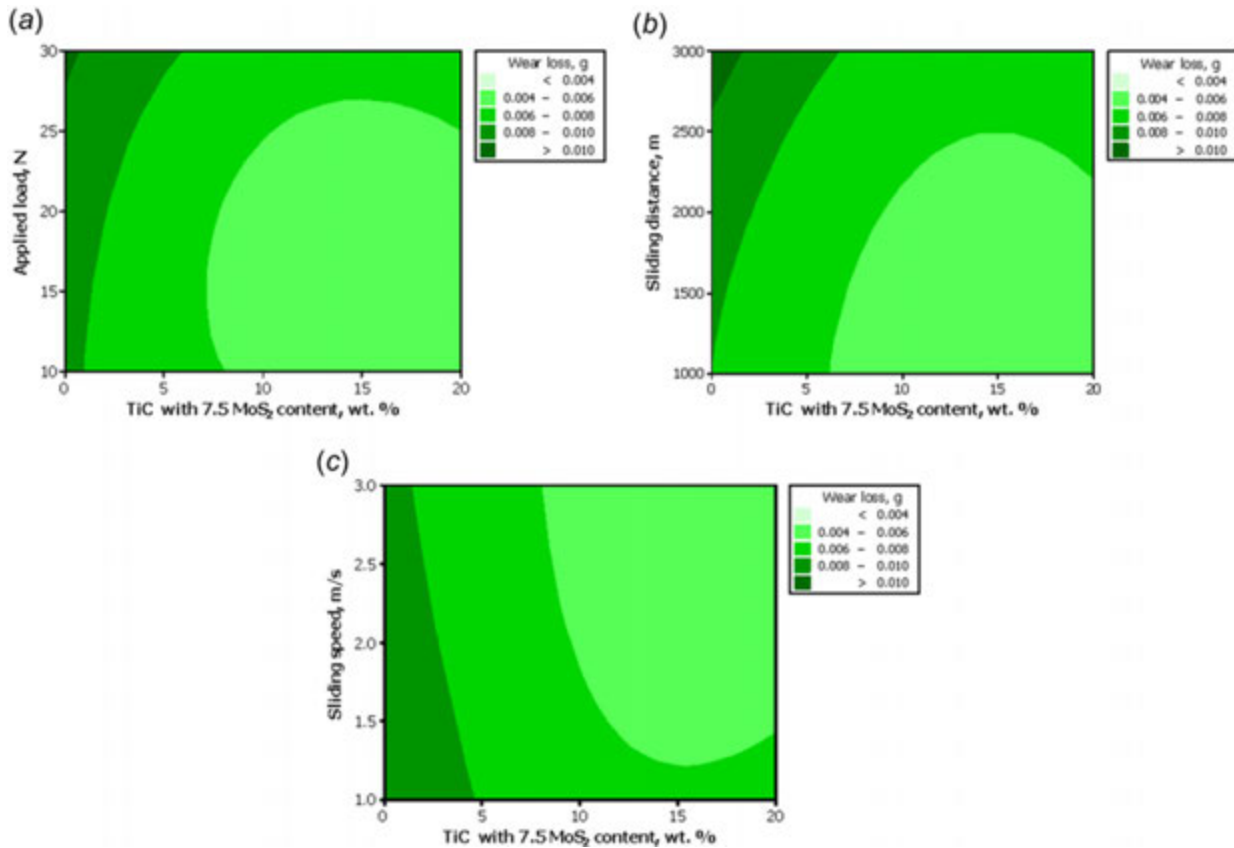


Fig. 27 Contour plot of wear loss effect between TiC reinforcement content and (a) applied load, (b) sliding distance, and (c) sliding speed reported by Narayanasamy and Selvakumar. Reproduced from Narayanasamy, P., Selvakumar, N., 2017. Effect of -mization of TiC on the -avior of Mg-MoS₂ composites. Journal of Tribology 139 (5), 051301. Available at: <https://doi.org/10.1115/1.4035383>.

prepare Mg based hybrid nanocomposites with a hierarchical configuration as shown in Fig. 23. The mechanical properties of hierarchical composites developed by Habibi *et al.* are listed in Table 11.

Recently, the effects of alumina and silicon carbide hybrid reinforcements on the properties powder metallurgy processed Mg-3Al-1Zn alloy were investigated by Rashad *et al.* (Rashad *et al.*, 2015b). In this study, the processing of Mg-hybrid composites involved blending the matrix and reinforcements particles in a wet medium, followed by the filtration, drying, and compaction of the composite powder blend (as illustrated in Fig. 24). The green composite compact was then sintered and extruded for microstructural and mechanical testing. While the results showed improvement in microhardness and tensile strength of the extruded hybrid composites at the expense of tensile strain with increasing reinforcement content, the tensile fracture strain was found to improve upon heat treatment (Table 12). Similar improvements in mechanical properties were also reported when (copper + graphene nanoplatelets) and (titanium + aluminum) hybrids were added to Mg (Rashad *et al.*, 2015c; Rashad *et al.*, 2015a).

Recently, Zhou *et al.* (Zhou *et al.*, 2019b) used the powder metallurgy method followed by hot extrusion to develop the multi-scaled micron SiC and carbon nanotubes (CNTs) reinforced AZ61 matrix composites as illustrated in Fig. 25. In this study, the

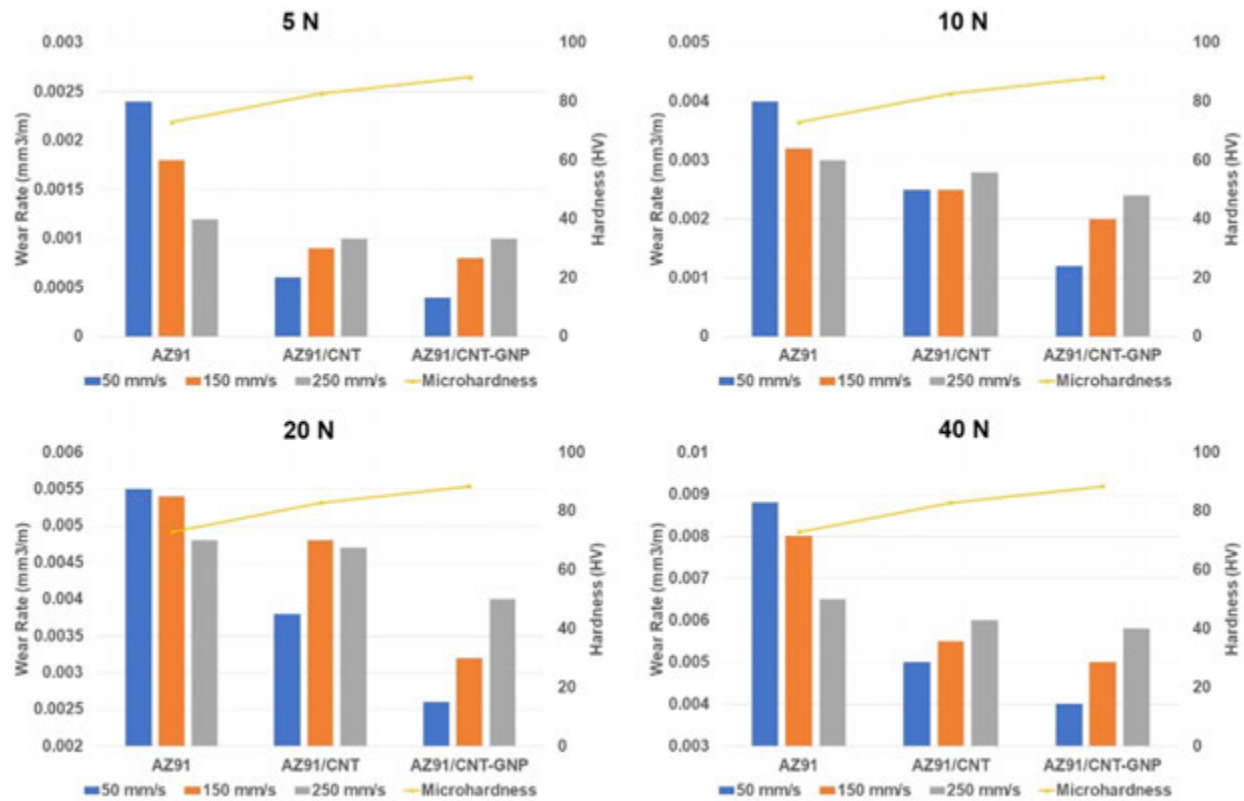


Fig. 28 Hardness and wear rates of AZ91/CNT-GNP hybrid composites reported by Turan *et al.* Modified from Turan, M.E., Zengin, H., Sun, Y., 2019. Dry sliding wear behavior of (MWCNT + GNPs) reinforced AZ91 magnesium matrix hybrid composites. *Metals and Materials International* 26, 541–550. Available at: <https://doi.org/10.1007/s12540-019-00338-8>.

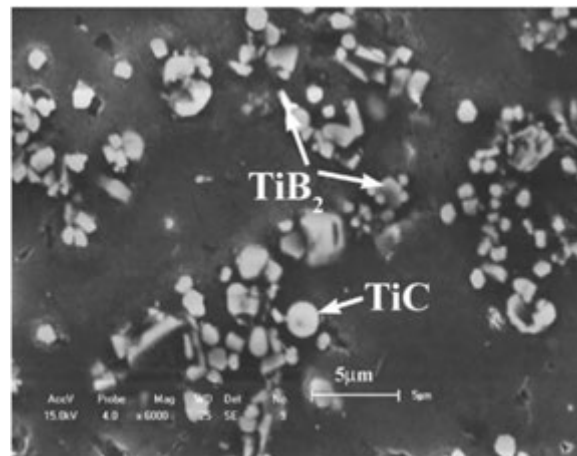


Fig. 29 High magnification SEM micrograph of the 5.5 wt% (TiB_2 – TiC)/AZ91 composite fabricated by adding (TiB_2 + TiC)-Al master alloy with 40 wt% Al. (Ma *et al.*, 2005).

CNTs were properly dispersed onto the surface of micron sized SiC particles and then integrated with AZ80 powders using the ball-milling process. The results of mechanical testing revealed ultra-high strength (~ 400 MPa) and ductility (8%) of AZ61/5SiC-0.5CNT due to the synergistic influence of grain refinement, load transfer and increased dislocation density in the matrix due to thermal mismatch accompanied by a weakened basal texture (Fig. 26, Table 13).

Some of the recent literatures also focussed on the tribological behavior of Mg based hybrid composites containing particle lubricants such as graphite, MoS_2 and CNTs. Narayanasamy and Selvakumar (Narayanasamy and Selvakumar, 2017) investigated the dry sliding wear behavior of powder metallurgy processed Mg composites reinforced with TiC and MoS_2 . While the wear test

Table 14 Mechanical and tribological properties of AZ91 alloy composites containing in-situ ($\text{TiB}_2 + \text{TiC}$) reinforcements

Material	Tensile properties			Hardness (HB)	Volumetric wear rate (10–10 m ³ /m)	
	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)		5 N	35 N
AZ91 alloy	82 ± 3	233 ± 0	6.0 ± 0.5	56	6.1166	19.9389
Mg/($\text{TiB}_2 + \text{TiC}$)	95 ± 2	298 ± 2	2.4 ± 0.4	79	2.6509	9.9477

Note: Ma, B.X. *et al.*, 2005. Fabrication of ($\text{TiB}_2 - \text{TiC}$)p/AZ91 magnesium matrix hybrid composite. Journal of Materials Science 40, 4501–4504. Available at: <https://doi.org/10.1007/s10853-005-0886-2>. Xiuqing, Z., *et al.*, 2005. The mechanical properties of magnesium matrix composites reinforced with ($\text{TiB}_2 + \text{TiC}$) ceramic particulates. Materials Letters 59 (17), 2105–2109. Available at: <https://doi.org/10.1016/j.matlet.2005.02.020>.

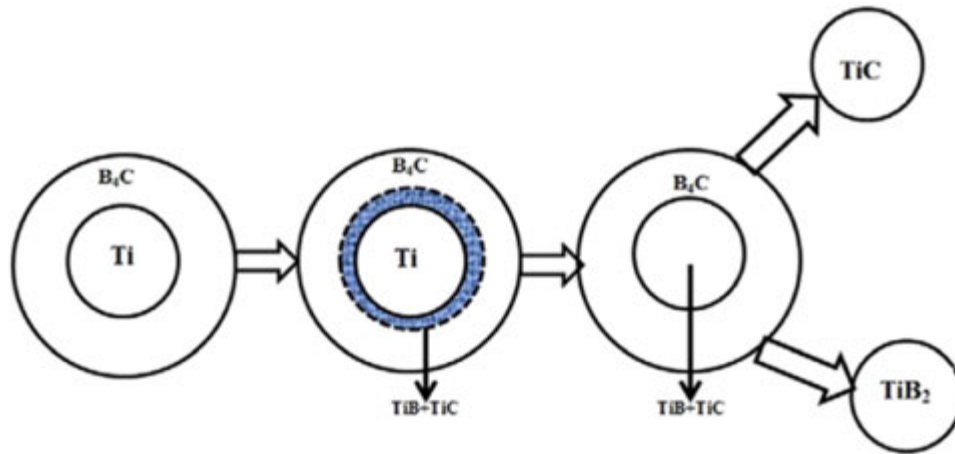


Fig. 30 Schematic diagram for reaction between Ti and B_4C particle. Reproduced from Sahoo, B.N., Panigrahi, S.K., 2018a. A study on the combined effect of in-situ (TiC-TiB_2) reinforcement and aging treatment on the yield asymmetry of magnesium matrix composite. Journal of Alloys and Compounds 737, 575–589. Available at: <https://doi.org/10.1016/j.jallcom.2017.12.027>.

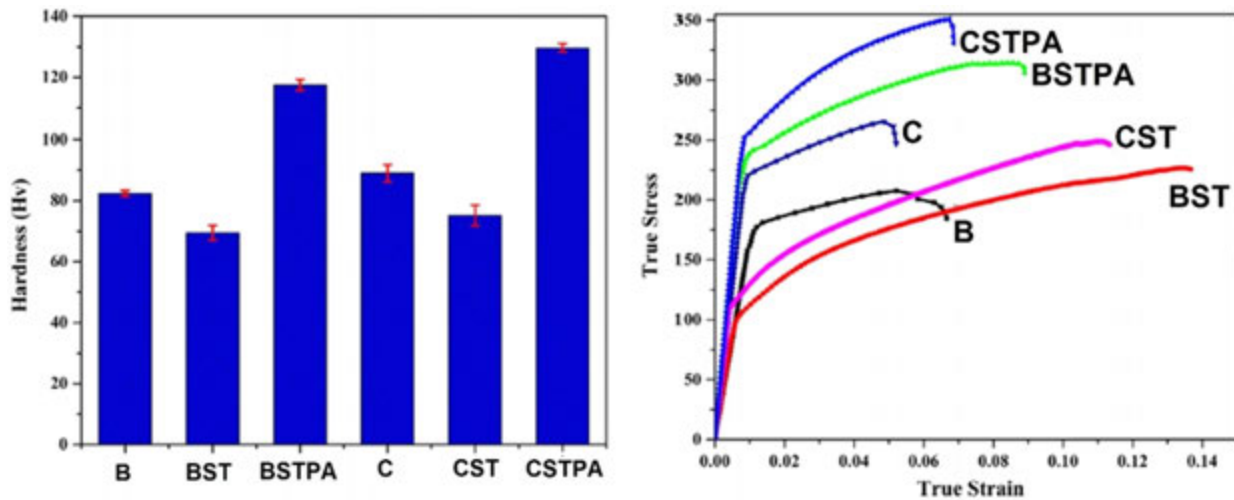


Fig. 31 Mechanical properties of AZ31/Ti- B_4C hybrid composites, Conditions: B - Base alloy; BST - Base alloy solution treated; BSTPA - Base alloy solution treated and peak aged (175°C for 60 h); C - Composite; CST - Composite solution treated; CSTPA - Composite solution treated and peak aged (175°C for 60 h), reported by Sahoo *et al.* Reproduced from Sahoo, B.N., Panigrahi, S.K., 2016. Synthesis, characterization and mechanical properties of in-situ (TiC-TiB_2) reinforced magnesium matrix composite. Materials and Design 109, 300–313. Available at: <https://doi.org/10.1016/j.matdes.2016.07.024>. Sahoo, B.N., Panigrahi, S.K., 2018b. Effect of in-situ (TiC-TiB_2) reinforcement on aging and mechanical behavior of AZ91 magnesium matrix composite. Materials Characterization 139, 221–232. Available at: <https://doi.org/10.1016/j.matchar.2018.03.002>. Sahoo, B.N., Panigrahi, S.K., 2018a. A study on the combined effect of in-situ (TiC-TiB_2) reinforcement and aging treatment on the yield asymmetry of magnesium matrix composite. Journal of Alloys and Compounds 737, 575–589. Available at: <https://doi.org/10.1016/j.jallcom.2017.12.027>. Sahoo, B.N., Panigrahi, S.K., 2019a. Deformation behavior and processing map development of AZ91 Mg alloy with and without addition of hybrid in-situ $\text{TiC} + \text{TiB}_2$ reinforcement. Journal of Alloys and Compounds 776, 865–882. Available at: <https://doi.org/10.1016/j.jallcom.2018.10.276>. Sahoo, B.N., Panigrahi, S.K., 2019b. Development of wear maps of in-situ $\text{TiC} + \text{TiB}_2$ reinforced AZ91 Mg matrix composite with varying microstructural conditions. Tribology International 135, 463–477. Available at: <https://doi.org/10.1016/j.triboint.2019.02.029>. Sahoo, B.N., *et al.*, 2018. Microstructural modification and its effect on strengthening mechanism and yield asymmetry of in-situ TiC-TiB_2 / AZ91 magnesium matrix composite. Materials Science and Engineering A 724, 269–282. Available at: <https://doi.org/10.1016/j.msea.2018.03.060>.

Table 15 Mechanical Properties of AZ31/Ti-B₄C hybrid composites reported by Sahoo *et al.*

Conditions	Tensile properties			Compressive properties			Yield ratio
	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)	Yield strength (MPa)	Ultimate strength (MPa)	Failure strain (%)	
Tested in rolling direction (RD)							
B	171	197	5.3	131	378	15.57	1.3
BST	95	198	14	76	271	17.5	1.25
BSTPA	225	291	7	184	381	15.97	1.22
C	203	253	6.8	177	396	12.94	1.14
CST	104	223	11.1	88	301	14.5	1.18
CSTPA	228	328	8.2	218	407	13.94	1.04
Tested in 45° to rolling direction (45°)							
B	163	246	8.0	120	339	15.04	1.36
BST	93	196	13.6	71	288	16.7	1.30
BSTPA	200	275	9.8	160	359	15.6	1.25
C	195	289	6.3	160	391	12.11	1.22
CST	102	216	10.7	86	287	13.9	1.18
CSTPA	218	354	8.0	191	403	13.38	1.14
Tested in transverse direction (TD)							
B	176	255	6.6	123	327	9.9	1.43
BST	91	177	11.8	62	267	12.82	1.46
BSTPA	173	271	8.6	146	346	11.10	1.18
C	175	273	5.6	142	373	9.35	1.23
CST	95	202	9.7	78	280	11.78	1.22
CSTPA	209	326	6.4	181	390	9.6	1.15
Condition:							
BBase alloy							
BSTBase alloy – solution treated							
BSTPA Base alloy – solution treated and peak aged (175°C for 60 h)							
CComposite							
CSTComposite – solution treated							
CSTPA Composite – solution treated and peak aged (175°C for 60 h)							

Condition:

BBase alloy

BSTBase alloy – solution treated

BSTPA Base alloy – solution treated and peak aged (175°C for 60 h)

CComposite

CSTComposite – solution treated

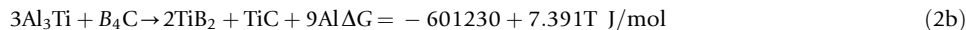
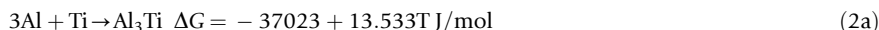
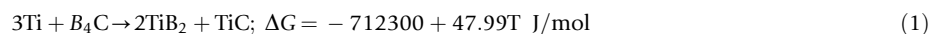
CSTPA Composite – solution treated and peak aged (175°C for 60 h)

Note: Sahoo, B.N., Panigrahi, S.K., 2016. Synthesis, characterization and mechanical properties of in-situ (TiC-TiB₂) reinforced magnesium matrix composite. *Materials and Design* 109, 300–313. Available at: <https://doi.org/10.1016/j.matdes.2016.07.024>. Sahoo, B.N., Panigrahi, S.K., 2018b. Effect of in-situ (TiC-TiB₂) reinforcement on aging and mechanical behavior of AZ91 magnesium matrix composite. *Materials Characterization* 139, 221–232. Available at: <https://doi.org/10.1016/j.matchar.2018.03.002>. Sahoo, B.N., Panigrahi, S.K., 2018a. A study on the combined effect of in-situ (TiC-TiB₂) reinforcement and aging treatment on the yield asymmetry of magnesium matrix composite. *Journal of Alloys and Compounds* 737, 575–589. Available at: <https://doi.org/10.1016/j.jallcom.2017.12.027>. Sahoo, B.N., Panigrahi, S.K., 2019a. Deformation behavior and processing map development of AZ91 Mg alloy with and without addition of hybrid in-situ TiC + TiB₂ reinforcement. *Journal of Alloys and Compounds* 776, 865–882. Available at: <https://doi.org/10.1016/j.jallcom.2018.10.276>. Sahoo, B.N., Panigrahi, S.K., 2019b. Development of wear maps of in-situ TiC + TiB₂ reinforced AZ91 Mg matrix composite with varying microstructural conditions. *Tribology International* 135, 463–477. Available at: <https://doi.org/10.1016/j.triboint.2019.02.029>. Sahoo, B.N., *et al.*, 2018. Microstructural modification and its effect on strengthening mechanism and yield asymmetry of in-situ TiC-TiB₂/ AZ91 magnesium matrix composite. *Materials Science and Engineering A* 724, 269–282. Available at: <https://doi.org/10.1016/j.msea.2018.03.060>.

results under dry sliding condition showed better wear resistance and reduced coefficient of friction for the hybrid composites due to the formation of a smooth MoS₂-rich tribo-layer, TiC content was found to be beneficial only up to 15%, beyond which the wear loss had the propensity to increase. In a similar study (Turan *et al.*, 2019), a best combination of mechanical and tribological properties were recorded for the AZ91/0.15 wt%CNT-0.15%GNP composite reinforced with multiple carbon-based reinforcements such as CNTs and GNPs (Fig. 28). Similar improvement in wear resistance was also reported in the case of Mg-SiC-Graphite hybrid composites (Soorya Prakash *et al.*, 2016). (Fig. 27).

Development of Mg Hybrid Composites Containing In-Situ Formed Reinforcements

The review of recent literatures also highlights the in-situ synthesis of hybrid (TiB₂ + TiC) reinforcement based on the solid-state chemical reactions between the Ti, B and C phases. Ma *et al.* (2005) and Xiuqing *et al.* (2005) used the self-propagating high temperature synthesis based powder metallurgy technique to prepare a master Al/(TiB₂-TiC) composite which was then re-melted and diluted using the stir casting method to produce AZ91/TiB₂-TiC hybrid composite with improved mechanical properties and wear resistance. The reactions between Ti, Al and B₄C phases were explained as follows:



The developed composites with in-situ ($\text{TiB}_2 + \text{TiC}$) particles (Fig. 29) displayed better mechanical properties (Xiuqing *et al.*, 2005) and wear resistance (Ma *et al.*, 2005) as shown in Table 14.

Sahoo and Panigrahi (Sahoo and Panigrahi, 2016, 2018a,b, 2019a,b; Sahoo *et al.*, 2018) also confirmed the in-situ formation of TiC and TiB_2 phases due to the interaction of Ti , and B_4C powders with molten Mg in $\text{AZ31/Ti-B}_4\text{C}$ composite as shown in Fig. 30. The developed composites were investigated for mechanical properties in terms of yield strength, yield asymmetry and deformation behavior in the as-cast and heat-treated condition, which showed improved ductility under heat-treated condition (Fig. 31 and Table 15).

Concluding Remarks

In this article, the research efforts made thus far on the development of magnesium-based metal matrix composites containing hybrid reinforcements are summarized. The processing techniques adopted so far include melt infiltration, squeeze casting, stir casting, friction stir processing, disintegrated melt deposition and powder metallurgy methods. While hybrid reinforcement additions were originally proposed as an economical alternative to replace only a small quantity of the expensive fiber reinforcement, the improvements in mechanical, creep and tribological properties of Mg alloys due to hybrid reinforcements are found to be comparable to that of the fiber or particle reinforced Mg composites.

In this perspective, a variety of other hybrid reinforcement addition such as the mixture of different length scale particles and the combination of ceramic and metallic reinforcements have been used to develop Mg based hybrid composites and the review of existing literature suggests that the benefits of hybrid reinforcement addition generally depends on the matrix composition, reinforcement morphology, their distribution, and the interfacial integrity between the matrix and reinforcements.

Although in most cases, hybrid reinforcement additions enhance the mechanical, tribological, thermal and impression creep characteristics, corrosion response is often compromised. Similarly, superior improvements in mechanical properties are achieved when a dilute volume fraction of nanoscale ceramic/metallic dispersions are introduced either alone or in combination with other fiber/particle reinforcements when compared to micron scale particles.

The pre-processing of hybrid reinforcements also has a positive influence on the interfacial characteristics and the mechanical properties of Mg -hybrid composites. Similar enhancement in interfacial bonding and mechanical properties are also found in case of Mg hybrid composites containing in-situ formed hybrid reinforcements wherein the chemical reactions between matrix and reinforcements facilitates the formation of multiple reinforcing phases with good interfacial integrity and effective load transfer.

While most hybrid reinforcements results in comparable mechanical properties as that of the matrix material or the composites reinforced with single reinforcement, the best set of mechanical properties (ultra-high tensile strength ($\sim 400 \text{ MPa}$) and moderate ductility (8%)) is reported in the case of CNT and SiC particles reinforced AZ61 composites prepared using the method of powder metallurgy followed by hot extrusion.

The hybrid reinforcement methodology is also considered to be beneficial for industrial/domestic waste recycling as a small amount of the same can effectively be used as functional hybrid reinforcements to develop environment friendly composites.

References

- Aathisugan, I., Razal Rose, A., Selwyn Jebadurai, D., 2017. Mechanical and wear behaviour of AZ91D magnesium matrix hybrid composite reinforced with boron carbide and graphite. *Journal of Magnesium and Alloys* 5 (1), 20–25. <https://doi.org/10.1016/j.jma.2016.12.004>.
- Arokiasamy, S., Anand Ronald, B., 2017. Experimental investigations on the enhancement of mechanical properties of magnesium-based hybrid metal matrix composites through friction stir processing. *International Journal of Advanced Manufacturing Technology* 93, 493–503. <https://doi.org/10.1007/s00170-017-0221-5>.
- Arokiasamy, S., Anand Ronald, B., 2018. Enhanced properties of magnesium based metal matrix composites via Friction Stir Processing. *Materials Today Proceedings* 5 (2), 6934–6939. <https://doi.org/10.1016/j.matpr.2017.11.355>.
- Asano, K., Yoneda, H., 2008a. Development of short alumina fibre and in situ Mg_2Si particle reinforced magnesium alloy hybrid composite with high temperature strength. *International Journal of Cast Metals Research* 21 (1–4), 239–245. <https://doi.org/10.1179/136404608x362025>.
- Asano, K., Yoneda, H., 2008b. High temperature properties of AZ91D magnesium alloy composite reinforced with short alumina fiber and Mg_2Si particle. *Materials Transactions* 49 (7), 1688–1693. <https://doi.org/10.2320/matertrans.MER2008092>.
- Avedesian, M.M., Baker, H., 1999. *ASM Specialty Handbook: Magnesium and Magnesium Alloys*. Materials Park, OH: ASM International.
- Babu, J.S.S., *et al.*, 2010. Fabrication and properties of magnesium (AM50)-based hybrid composites with graphite nanofiber and alumina short fiber. *Journal of Composite Materials* 44 (8), 971–987. <https://doi.org/10.1177/0021998309349548>.
- Babu, J.S.S., Kang, C.G., 2010. Nanoindentation behaviour of aluminium based hybrid composites with graphite nanofiber/alumina short fiber. *Materials and Design* 31 (10), 4881–4885. <https://doi.org/10.1016/j.matdes.2010.05.029>.
- Fida Hassan, S., *et al.*, 2015a. Effect of copper nano particles on high temperature tensile behavior of $\text{Mg-YMg-Y}_2\text{O}_3$ nanocomposite. *Metals and Materials International*. (3), <https://doi.org/10.1007/s12540-015-4188-1>.
- Fida Hassan, S., *et al.*, 2015b. Magnesium-nickel composite: Preparation, microstructure and mechanical properties. *Journal of Alloys and Compounds* 646, 333–338. <https://doi.org/10.1016/j.jallcom.2015.06.099>.

- Fida Hassan, S., *et al.*, 2016. Magnesium nanocomposite: increasing copperisation effect on high temperature tensile properties. *Powder Metallurgy*. <https://doi.org/10.1080/00325899.2015.1109816>.
- Gupta, M., Sharon, N.M.L., 2010. Magnesium Alloys, and Magnesium Composites. Wiley. <https://doi.org/10.1002/9780470905098>.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 3–46. <https://doi.org/10.1016/j.matchar.2015.04.015>.
- Habibi, M.K., *et al.*, 2011. Using integrated hybrid (Al + CNT) reinforcement to simultaneously enhance strength and ductility of magnesium. *Composites Science and Technology* 71 (5), 734–741. <https://doi.org/10.1016/j.compscitech.2011.01.021>.
- Habibi, M.K., Joshi, S.P., Gupta, M., 2011. Development of hierarchical magnesium composites using hybrid microwave sintering. *Journal of Microwave Power and Electromagnetic Energy* 45 (3), 112–120. <https://doi.org/10.1080/08327823.2011.11689805>.
- Habibi, M.K., *et al.*, 2012a. Differentiating the mechanical response of hierarchical magnesium nano-composites as a function of temperature. *Materials and Design* 42, 102–110. <https://doi.org/10.1016/j.matdes.2012.05.037>.
- Habibi, M.K., Hamouda, A.M.S., Gupta, M., 2012b. Enhancing tensile and compressive strength of magnesium using ball milled Al + CNT reinforcement. *Composites Science and Technology* 72 (2), 290–298. <https://doi.org/10.1016/j.compscitech.2011.11.015>.
- Habibi, M.K., Joshi, S.P., Gupta, M., 2010. Hierarchical magnesium nano-composites for enhanced mechanical response. *Acta Materialia* 58 (18), 6104–6114. <https://doi.org/10.1016/j.actamat.2010.07.028>.
- Habibi, M.K., Hamouda, A.S., Gupta, M., 2013a. Hybridizing boron carbide (B4C) particles with aluminum (Al) to enhance the mechanical response of magnesium based nano-composites. *Journal of Alloys and Compounds* 550, 83–93. <https://doi.org/10.1016/j.jallcom.2012.09.128>.
- Habibi, M.K., Hamouda, A.S., Gupta, M., 2013b. Using hierarchical composite approach to improve mechanical response of Mg and Mg-Bi₂O₃ nano-composites. *Materials and Design* 49, 627–637. <https://doi.org/10.1016/j.matdes.2013.02.028>.
- Habibi, M.K., *et al.*, 2010. Tensile strength and ductility improvement of magnesium by using ball milled Al-CNT particles as reinforcement. In: *Proceedings of the Materials Science and Technology Conference and Exhibition*. MS and T'10.
- Hassan, S.F., *et al.*, 2016. Microwave sintered magnesium nanocomposite: Hybrid (Y₂O₃ + Ni) nano-size reinforcement and ensile properties. *Advanced Composites Letters* 25 (4), 103–107. <https://doi.org/10.1177/096369351602500404>.
- Hassan, S.F., Gupta, M., 2002. Development of ductile magnesium composite materials using titanium as reinforcement. *Journal of Alloys and Compounds* 345 (1-2), 246–251. [https://doi.org/10.1016/S0925-8388\(02\)00413-9](https://doi.org/10.1016/S0925-8388(02)00413-9).
- Ibrahim, I.A., Mohamed, F.A., Lavernia, E.J., 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science* 26, 1137–1156. <https://doi.org/10.1007/BF00544448>.
- Kainer, K.U., *et al.*, 2010. Status of the development of creep resistant magnesium materials for automotive applications. *Materials Science Forum* 638 (642), 73–80. <https://doi.org/10.4028/www.scientific.net/MSF.638-642.73>. March 2016.
- Kumar, S., Dieringa, H., Kainer, K.U., 2005. Effect of particulate content on the thermal cycling behaviour of the magnesium alloy based hybrid composites. *Composites Part A Applied Science and Manufacturing* 36 (3), 321–325. <https://doi.org/10.1016/j.compositesa.2004.07.005>.
- Kumar, S., Dieringa, H., Kainer, K.U., 2007. Thermal cycling behaviour of the magnesium alloy based hybrid composites in the transverse direction. *Materials Science and Engineering A* 454-455, 367–370. <https://doi.org/10.1016/j.msea.2006.11.041>.
- Lu, D., Jiang, Y., Zhou, R., 2013. Wear performance of nano-Al₂O₃ particles and CNTs reinforced magnesium matrix composites by friction stir processing. *Wear* 305 (1-2), 286–290. <https://doi.org/10.1016/j.wear.2012.11.079>.
- Ma, B.X., *et al.*, 2005. Fabrication of (TiB₂ - TiC)/AZ91 magnesium matrix hybrid composite. *Journal of Materials Science* 40, 4501–4504. <https://doi.org/10.1007/s10853-005-0886-2>.
- Malaki, M., *et al.*, 2019. Advanced metal matrix nanocomposites. *Metals* 93. <https://doi.org/10.3390/met9030330>.
- Mondal, A.K., Kumar, S., 2008. Impression creep behaviour of magnesium alloy-based hybrid composites in the longitudinal direction. *Composites Science and Technology* 68 (15-16), 3251–3258. <https://doi.org/10.1016/j.compscitech.2008.08.007>.
- Mondal, A.K., Kumar, S., 2009a. Dry sliding wear behaviour of magnesium alloy based hybrid composites in the longitudinal direction. *Wear* 267 (1-4), 458–466. <https://doi.org/10.1016/j.wear.2008.12.036>.
- Mondal, A.K., Kumar, S., 2009b. Impression creep behaviour of magnesium alloy-based hybrid composites in the transverse direction. *Composites Science and Technology* 69 (10), 1592–1598. <https://doi.org/10.1016/j.compscitech.2009.02.038>.
- Mondal, A.K., Kumar, S., 2014. Dry sliding wear behaviour of magnesium alloy based hybrid composites in transverse direction. In: *Materials Science Forum*. (783-786), 1530. <https://doi.org/10.4028/www.scientific.net/msf.783-786.1530>.
- Mondal, A.K., Blawert, C., Kumar, S., 2015. Corrosion behaviour of creep-resistant AE42 magnesium alloy-based hybrid composites developed for powertrain applications. *Materials and Corrosion* 6 (10), 1150–1158. <https://doi.org/10.1002/maco.201408071>.
- Mordike, B.L., Ebert, T., 2001. Magnesium Properties – Applications – Potential. *Materials Science and Engineering A* 3021, 37–45. [https://doi.org/10.1016/S0921-5093\(00\)01351-4](https://doi.org/10.1016/S0921-5093(00)01351-4).
- Narayanasamy, P., Selvakumar, N., 2017. Effect of –mization of TiC on the –avior of Mg-MoS₂ composites. *Journal of Tribology* 139 (5), 051301. <https://doi.org/10.1115/1.4035383>.
- Nguyen, Q.B., *et al.*, 2011. Enhancing strength and hardness of AZ31B through simultaneous addition of nickel and nano-Al₂O₃ particulates. *Materials Science and Engineering A* 528 (3), 888–894. <https://doi.org/10.1016/j.msea.2010.10.021>.
- Nguyen, Q.B., *et al.*, 2012a. Simultaneous effect of nano-Al₂O₃ and micrometre Cu particulates on microstructure and mechanical properties of magnesium alloy AZ31. *Materials Science and Technology* 28 (2), 227–233. <https://doi.org/10.1179/1743284711Y.0000000023>.
- Nguyen, Q.B., Tun, K.S., Gupta, M., 2012b. Effect of nano-alumina and copper micron size particulates on microstructure and mechanical properties of magnesium alloy AZ31. *Magnesium Technology*. 187–189. https://doi.org/10.1007/978-3-319-48203-3_35.
- Nguyen, Q.B., Gupta, M., 2010. Enhancing mechanical response of AZ31B using Cu + nano-Al₂O₃ addition. *Materials Science and Engineering A* 527 (6), 1411–1416. <https://doi.org/10.1016/j.msea.2009.11.002>.
- Olalekan, O., 2016. Development of Magnesium Based Hybrid Nanocomposite. Saudi Arabia: King Fahd University of Petroleum and Minerals, <http://search.proquest.com/openview/507fd960dc966269fb6dbe8c917a1b4d/1?pq-origsite=gscholar&cbl=2026366&diss=y>.
- Pekguleryuz, M., Kainer, K., Kaya, A.A., 2013. Fundamentals of Magnesium Alloy Metallurgy. Wiley. <https://doi.org/10.1533/9780857097293>.
- Rashad, M., Pan, F., Asif, M., *et al.*, 2015a. Improved mechanical proprieties of "magnesium based composites" with titanium-aluminum hybrids. *Journal of Magnesium and Alloys* 3 (1), 1–9. <https://doi.org/10.1016/j.jma.2014.12.010>.
- Rashad, M., Pan, F., Guo, W., *et al.*, 2015b. Effect of alumina and silicon carbide hybrid reinforcements on tensile, compressive and microhardness behavior of Mg-3Al-1Zn alloy. *Materials Characterization* 106, 382–389. <https://doi.org/10.1016/j.matchar.2015.06.033>.
- Rashad, M., *et al.*, 2015c. Improved mechanical properties of magnesium-graphene composites with copper-graphene hybrids. *Materials Science and Technology United Kingdom* 31 (12), <https://doi.org/10.1179/1743284714Y.00000000726>.
- Sahoo, B.N., *et al.*, 2018. Microstructural modification and its effect on strengthening mechanism and yield asymmetry of in-situ TiC-TiB₂/ AZ91 magnesium matrix composite. *Materials Science and Engineering A* 724, 269–282. <https://doi.org/10.1016/j.msea.2018.03.060>.
- Sahoo, B.N., Panigrahi, S.K., 2016. Synthesis, characterization and mechanical properties of in-situ (TiC-TiB₂) reinforced magnesium matrix composite. *Materials and Design* 109, 300–313. <https://doi.org/10.1016/j.matdes.2016.07.024>.

- Sahoo, B.N., Panigrahi, S.K., 2018a. A study on the combined effect of in-situ (TiC-TiB₂) reinforcement and aging treatment on the yield asymmetry of magnesium matrix composite. *Journal of Alloys and Compounds* 737, 575–589. <https://doi.org/10.1016/j.jallcom.2017.12.027>.
- Sahoo, B.N., Panigrahi, S.K., 2018b. Effect of in-situ (TiC-TiB₂) reinforcement on aging and mechanical behavior of AZ91 magnesium matrix composite. *Materials Characterization* 139, 221–232. <https://doi.org/10.1016/j.matchar.2018.03.002>.
- Sahoo, B.N., Panigrahi, S.K., 2019a. Deformation behavior and processing map development of AZ91 Mg alloy with and without addition of hybrid in-situ TiC + TiB₂ reinforcement. *Journal of Alloys and Compounds* 776, 865–882. <https://doi.org/10.1016/j.jallcom.2018.10.276>.
- Sahoo, B.N., Panigrahi, S.K., 2019b. Development of wear maps of in-situ TiC + TiB₂ reinforced AZ91 Mg matrix composite with varying microstructural conditions. *Tribology International* 135, 463–477. <https://doi.org/10.1016/j.triboint.2019.02.029>.
- Sankaranarayanan, S., *et al.*, 2013. Effect of hybridizing micron-sized Ti with nano-sized SiC on the microstructural evolution and mechanical response of Mg-5.6Ti composite. *Journal of Alloys and Compounds* 575, 207–217. <https://doi.org/10.1016/j.jallcom.2013.04.095>.
- Sankaranarayanan, S., *et al.*, 2014. Microstructural evolution and mechanical properties of Mg composites containing nano-B₄C hybridized micro-Ti particulates. *Materials Chemistry and Physics* 143 (3), 1178–1190. <https://doi.org/10.1016/j.matchemphys.2013.11.019>.
- Sankaranarayanan, S., Gupta, M., 2015a. Review on mechanical properties of magnesium (nano)composites developed using energy efficient microwaves. *Powder Metallurgy* 583, 183–192. <https://doi.org/10.1179/1743290115Y.0000000009>.
- Sankaranarayanan, S., Jayalakshmi, S., Gupta, M., 2011a. Effect of addition of mutually soluble and insoluble metallic elements on the microstructure, tensile and compressive properties of pure magnesium. *Materials Science and Engineering A* 530 (1), 149–160. <https://doi.org/10.1016/j.msea.2011.09.066>.
- Sankaranarayanan, S., Jayalakshmi, S., Gupta, M., 2011b. Effect of ball milling the hybrid reinforcements on the microstructure and mechanical properties of Mg-(Ti + n-Al₂O₃) composites. *Journal of Alloys and Compounds* 509 (26), 7229–7237. <https://doi.org/10.1016/j.jallcom.2011.04.083>.
- Schröder, J., Kainer, K.U., 1991. Magnesium-base hybrid composites prepared by liquid infiltration. *Materials Science and Engineering A* 135, 33–36. [https://doi.org/10.1016/0921-5093\(91\)90532-R](https://doi.org/10.1016/0921-5093(91)90532-R).
- Seetharaman, S., *et al.*, 2012. Influence of micron-Ti and Nano-Cu additions on the microstructure and mechanical properties of pure magnesium. *Metals* 2 (3), 274–291. <https://doi.org/10.3390/met2030274>.
- Sharma, S., *et al.*, 2019. Influence of tool rotation speeds on mechanical and morphological properties of friction stir processed nano hybrid composite of MWCNT-Graphene-AZ31 magnesium. *Journal of Magnesium and Alloys* 7 (3), 487–500. <https://doi.org/10.1016/j.jma.2019.07.001>.
- Sinha, S.K., Reddy, S.U., Gupta, M., 2006. Scratch hardness and mechanical property correlation for Mg/SiC and Mg/SiC/Ti metal-matrix composites. *Tribology International* 39 (2), 184–189. <https://doi.org/10.1016/j.triboint.2005.04.017>.
- Soorya Prakash, K., *et al.*, 2016. Mechanical and wear behaviour of Mg-SiC-Gr hybrid composites. *Journal of Magnesium and Alloys* 4 (3), 197–206. <https://doi.org/10.1016/j.jma.2016.08.001>.
- Srivatsan, T.S., Sudarshan, T.S., Lavernia, E.J., 1995. Processing of discontinuously-reinforced metal matrix composites by rapid solidification. *Progress in Materials Science* 39 (4-5), 317–409. [https://doi.org/10.1016/0079-6425\(95\)00003-8](https://doi.org/10.1016/0079-6425(95)00003-8).
- Svoboda, M., *et al.*, 2007. Microstructure and creep behaviour of magnesium hybrid composites. *Materials Science and Engineering A* 562 (1-2), 220–224. <https://doi.org/10.1016/j.msea.2006.02.466>.
- Thakur, S.K., Balasubramanian, K., Gupta, M., 2007a. Microwave synthesis and characterization of magnesium based composites containing nanosized SiC and hybrid (SiC + Al₂O₃) reinforcements. *Journal of Engineering Materials and Technology, Transactions of the ASME* 129 (2), 194–199. <https://doi.org/10.1115/1.2400279>.
- Thakur, S.K., Kwee, G.T., Gupta, M., 2007b. Development and characterization of magnesium composites containing nano-sized silicon carbide and carbon nanotubes as hybrid reinforcements. *Journal of Materials Science* 42, 10040–10046. <https://doi.org/10.1007/s10853-007-2004-0>.
- Tun, K.S., *et al.*, 2012. Enhancing tensile and compressive strengths of magnesium using nanosize (Al₂O₃ + Cu) hybrid reinforcements. *Journal of Composite Materials* 46 (15), 1879–1887. <https://doi.org/10.1177/0021998311427767>.
- Tun, K.S., *et al.*, 2013. Tensile and Compressive Responses of Ceramic and Metallic Nanoparticle Reinforced Mg Composites. *Materials* 6 (5), 1826–1839. <https://doi.org/10.3390/ma6051826>.
- Tun, K.S., Gupta, M., 2009. Development of magnesium/(yttria + nickel) hybrid nanocomposites using hybrid microwave sintering: Microstructure and tensile properties. *Journal of Alloys and Compounds* 487 (1-2), 76–82. <https://doi.org/10.1016/j.jallcom.2009.07.117>.
- Tun, K.S., Gupta, M., 2010a. Compressive deformation behavior of Mg and Mg/(Y₂O₃ + Ni) nanocomposites. *Materials Science and Engineering A* 527 (21-22), 5550–5556. <https://doi.org/10.1016/j.msea.2010.05.025>.
- Tun, K.S., Gupta, M., 2010b. Role of microstructure and texture on compressive strength improvement of Mg/(Y₂O₃ + Cu) hybrid nanocomposites. *Journal of Composite Materials* 44 (25), 3033–3050. <https://doi.org/10.1177/0021998310369591>.
- Turan, M.E., Zengin, H., Sun, Y., 2019. Dry sliding wear behavior of (MWCNT + GNPs) reinforced AZ91 magnesium matrix hybrid composites. *Metals and Materials International* 26, 541–550. <https://doi.org/10.1007/s12540-019-00338-8>.
- Ugandhar, S., Gupta, M., Sinha, S.K., 2006. Effect of hybrid metallic and ceramic reinforcements on the properties of pure magnesium. *Solid State Phenomena* 111, 79–82. <https://doi.org/10.4028/www.scientific.net/SSP.111.79>.
- Wong, W.L.E., Gupta, M., 2007. Development of Mg/Cu nanocomposites using microwave assisted rapid sintering. *Composites Science and Technology* 677–678, 1541–1552. <https://doi.org/10.1016/j.compscitech.2006.07.015>.
- Xiuqing, Z., *et al.*, 2005. The mechanical properties of magnesium matrix composites reinforced with (TiB₂ + TiC) ceramic particulates. *Materials Letters* 59 (17), 2105–2109. <https://doi.org/10.1016/j.matlet.2005.02.020>.
- Zhang, X., Zhang, Q., Hu, H., 2014. Tensile behaviour and microstructure of magnesium AM60-based hybrid composite containing Al₂O₃ fibres and particles. *Materials Science and Engineering A* 607, 269–276. <https://doi.org/10.1016/j.msea.2014.03.069>.
- Zhou, J., *et al.*, 2017. Processing and properties of as-cast magnesium AM60-based composite containing alumina nano particles and micron fibres. *Minerals, Metals and Materials Series*. https://doi.org/10.1007/978-3-319-52392-7_79.
- Zhou, J., *et al.*, 2019a. As-cast magnesium AM60-based hybrid nanocomposite containing alumina fibres and nanoparticles: Microstructure and tensile behavior. *Materials Science and Engineering A* 740–741, 305–314. <https://doi.org/10.1016/j.msea.2017.10.070>.
- Zhou, M.Y., *et al.*, 2019b. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. *Materials Science and Engineering A* 768, 138447. <https://doi.org/10.1016/j.msea.2019.138447>.
- Zhou, X., *et al.*, 2012. Tensile mechanical properties and strengthening mechanism of hybrid carbon nanotube and silicon carbide nanoparticle reinforced magnesium alloy composites. *Journal of Nanomaterials*. 851862. <https://doi.org/10.1155/2012/851862>.

Metal Based Composites With Metastable/Amorphous Reinforcements

Penchal Reddy Matli and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Composite is defined as a judicious combination of two or more different materials to achieve distinctive properties that cannot be achieved by any of its components individually (Rajak *et al.*, 2019). Traditional engineering sectors such as automotive, sports and aerospace are specially looking for lightweight composites (Avedesian and Baker, 1999; Ibrahim *et al.*, 1991; Safri *et al.*, 2018; Surappa, 2003). Presently, the automotive industry manufacturers have started using lightweight composites more aggressively. For most components made of lightweight composites, durability and strength plays a significant role while considering cost savings due to the high cost of fuel and the need to mitigate greenhouse gas emissions. Further, advancement in processing methods has enabled discontinuously reinforced composites to be produced in large scales (Rajan *et al.*, 1998; Ramanathan *et al.*, 2019).

Based on the matrix material, the composites can be categorized as Ceramic Matrix Composites (CMCs), Polymer Matrix Composites (PMCs) and Metal Matrix Composites (MMCs). Among these categories of composites, MMCs exhibit superior combination of mechanical, thermal properties and lightness making them particularly suitable for automobile body parts such as rotors and brake drums (Ekka *et al.*, 2014; Miracle, 2005). Commonly used lightweight metallic matrices, ceramic and amorphous reinforcements are shown in Fig. 1.

By the incorporation of a strong and compatible reinforcement, characteristics of metallic matrix such as stiffness, strength, wear resistance, elastic modulus and corrosion resistance can be enhanced. Al and Mg being the lightest structural metals are most sought after for the production of light-weight structures. Besides being light, Al and Mg based materials also exhibit excellent machinability, good castability, and superior mechanical properties besides being cost effective. As a result, they are also being looked as functional materials in electronic packaging, electricity transmission in addition to automotive/space/aerospace/military and sport sectors (Gupta and Sharon, 2010; Matli *et al.*, 2020; Prabu *et al.*, 2006; Reddy *et al.*, 2019; Zheng *et al.*, 2013). The current and prospective applications of MMCs in various commercial/industrial sectors (Ramanathan *et al.*, 2019) are shown in Fig. 2.

Conventionally, metallic matrices are strengthened by ceramic reinforcements such as titanium oxide (TiO₂), aluminum oxide (Al₂O₃), boron carbide (B₄C), silicon carbide (SiC), aluminum nitride (AlN), and graphite (C) (Meenashisundaram *et al.*, 2015; Reddy *et al.*, 2017a,b; Ubaid *et al.*, 2017; Xiang *et al.*, 2016). Using ceramic based reinforcements, MMCs have attained many of the targeted application driven properties. However, the major limitation of MMCs particularly with micron size reinforcements is their low ductility, which can be attributed primarily due to particle breakage and poor interfacial characteristics (El-Labban *et al.*, 2016; Hwu *et al.*, 1996). While the particle breakage is size dependent, poor interfacial characteristics can be attributed to poor wettability between the matrix and the reinforcement particles. Owing to this drawback, particle agglomeration and interfacial defects occur, which have limited the utilization of MMCs in commercial/industrial applications (Dorward and Pritchett, 1988; Miracle, 2005; Rawal, 2001). As a promising solution to overcome the existing limitations (e.g., low ductility) of MMCs, a new class of reinforcements, namely metallic amorphous alloys was proposed.

Metallic amorphous alloys are a new class of materials that inherently exhibit superior mechanical properties (Inoue, 2001). This is because of their structure (i.e., random or short-range atomic order), and thermal behavior (i.e. the presence of glass transition temperature (T_g) and crystallization temperature (T_x)) (Zhou *et al.*, 2020) as shown in Fig. 3. Due to their unique structure, amorphous alloys deliver large elastic strain limit (~1 to 2%), high hardness and strength (~1–2 GPa) and high corrosion resistance (Inoue, 2001) when compared to the conventional materials. As a result of their high strain limit and high strength, metallic glasses are natural candidates for use as reinforcement especially at micron length scale in metallic matrices.

Since the early 2000s, metallic glass reinforcements have gradually being recognized as promising reinforcements in metallic matrices (Jayalakshmi *et al.*, 2018; Jayalakshmi and Gupta, 2015; Scudino *et al.*, 2008; Yu *et al.*, 2006). Due to their metallic nature, they are easily wetted and exhibit good interfacial bonding with the matrix (Khan *et al.*, 2018). With the use of Al-, Zr-, Fe-, Ni-, Cu- and Mg- based metallic glass particles (Guan *et al.*, 2020; Jayalakshmi *et al.*, 2014; Scudino *et al.*, 2009; Wang *et al.*, 2014b; Yuan *et al.*, 2014; Zhang *et al.*, 2018) as reinforcement, several studies have reported improvement in mechanical properties of metallic matrices.

In this article, emphasis is placed on Al and Mg matrices reinforced with different amorphous metallic particles. Synthesis methods, microstructure and mechanical properties of these composites are presented in forthcoming sections.

Synthesis of Metallic Amorphous Particles

At present, Powder metallurgy stood as the dominant manufacturing technique for the fabrication of industrial parts. In the final quarter of 20th century, PM has a rapid growth due to evolution of novel material processing phenomenons like rapid solidification process (RSP), mechanical alloying (MA) etc., for manufacturing powder. The metallic glasses have broadly manufactured by the mechanical alloying from the above technique.

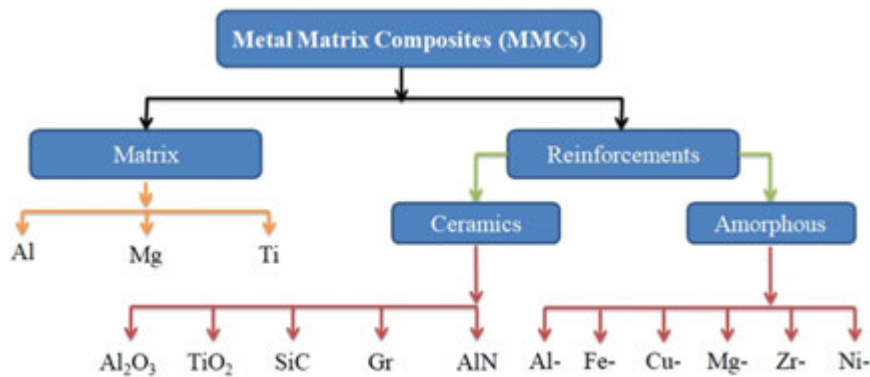


Fig. 1 Typical light metals and ceramics and amorphous reinforcements used for weight critical MMCs.

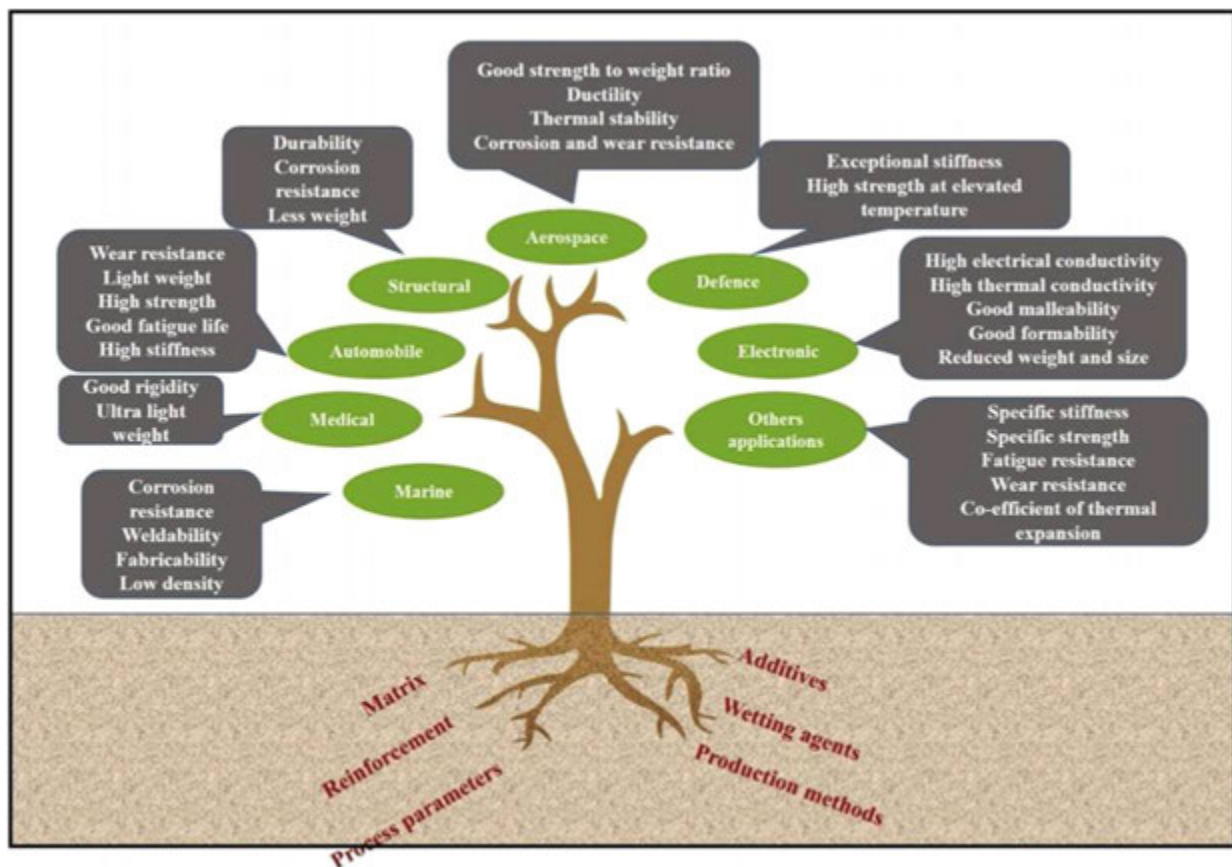


Fig. 2 Applications of MMCs in various fields.

Mechanical alloying is one of the powder metallurgy processes that involve repeated cold welding, fracturing, and rewelding of metallic powder particles. Due to solid-state inter diffusion reactions, amorphous structure occurred in mechanical alloying. [Fig. 4](#) represents the transformation of crystalline to amorphous phase using high energy mechanical alloying ([Suryanarayana, 2001](#)).

Fabrication of MMCs With Amorphous Particles

The metal matrix composites require metals in solid and liquid state for their fabrication. There is the possibility of coexistence of solid and liquid forms of the metal in the semi solid process. Till now, all the researchers produced fully amorphous reinforced

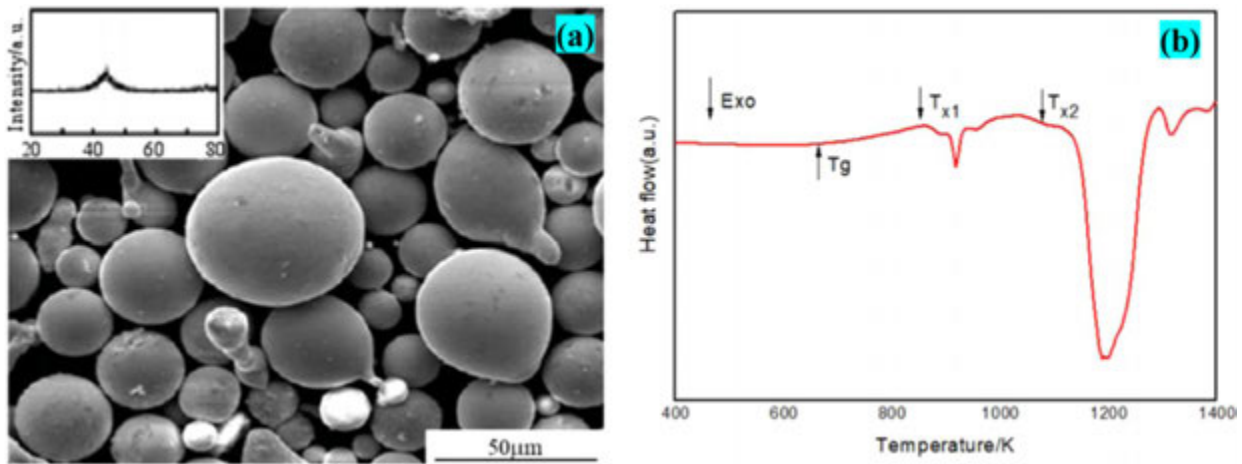


Fig. 3 Morphology, XRD pattern and DSC trace of $\text{Fe}_{52}\text{Cr}_{15}\text{Mo}_{26}\text{C}_3\text{B}_1\text{Y}_3$ amorphous powder.

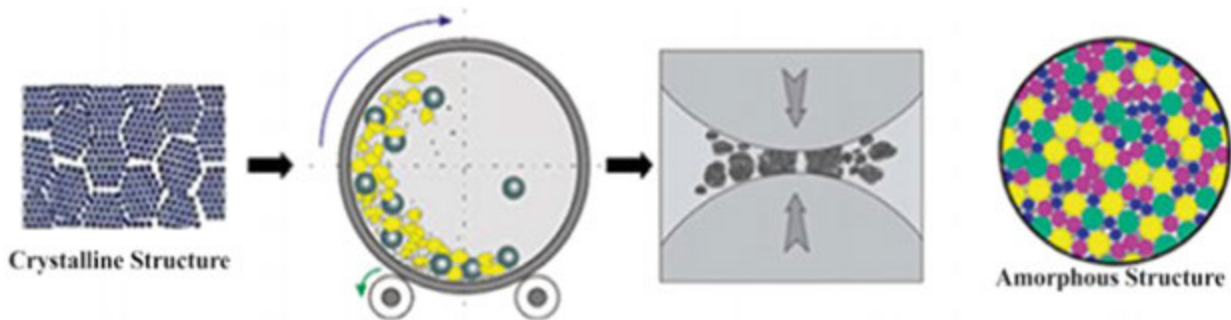


Fig. 4 Schematic diagram representing the transformation of crystalline to amorphous.

Al/Mg matrix composites using solid and liquid metallurgy routes (Jayalakshmi *et al.*, 2018). Some of the most common fabrication methods used by different researchers are described below.

Conventional and Advanced Processing Methods

Squeeze casting infiltration (SCI)

In this process, metal composites were fabricated by the infiltration of a molten alloy in amorphous particle preform, followed by solidification (Lee *et al.*, 2004).

By applying the hydraulic pressure or vacuum, the infiltration of molten metal in the preform was achieved. The production of metal composites by using the casting infiltration has increased gradually. The schematic representation of this process (Ramanathan *et al.*, 2019) is shown in Fig. 5. It was the first report on the synthesis and properties of the novel Al composites containing Ni–Nb–Ta alloy metallic glass particles (Lee *et al.*, 2004).

Compocasting (CS)

In the compocasting technique (Gladston *et al.*, 2017), preheated reinforcement particles are added into semi solid metal at predetermined temperature and dispersed using stirring. The semisolid slurry is poured in a die and solidified. The solidified billet can be further processed using secondary processing techniques (Fig. 6). This method has been shown to be successful in realizing good distribution of reinforcement particles, low porosity and fairly homogeneous and globular microstructure. The low processing temperature and production cycle time enhances the die life significantly and was the main advantages of compocasting.

Blend-compact-sinter method (BCS)

Using this method, metal matrix composites were synthesized by blending the matrix and amorphous reinforcement followed by compaction and sintering. The temperature of sintering is normally controlled so as to retain the amorphous nature of reinforcement. Using this method, composites with high volume percent of reinforcement (> 40%) can be developed. This process was successfully used to develop Al matrix composites containing Zr-based and Ni-based glassy particles (Yu *et al.*, 2006; Scudino *et al.*, 2009).

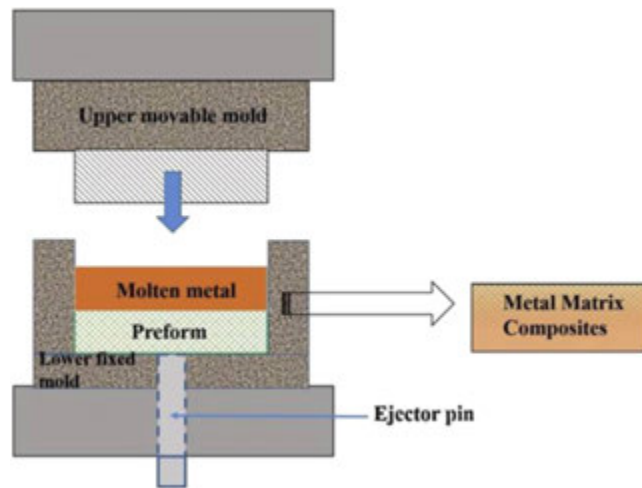


Fig. 5 Schematic diagram of squeeze casting infiltration method.

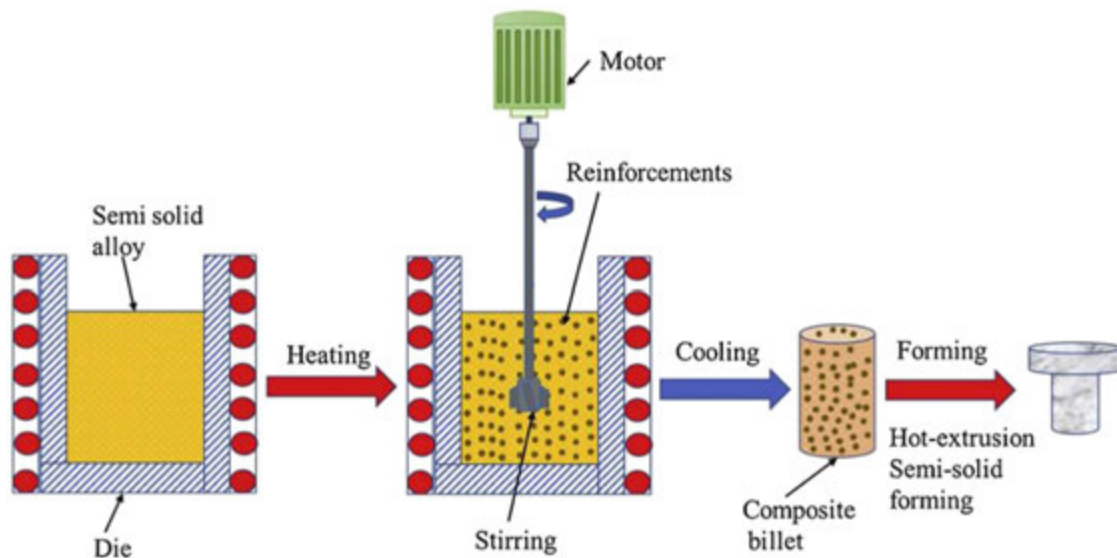


Fig. 6 Schematic diagram showing different steps in compocasting.

Powder metallurgy accompanied with microwave sintering (MWS)

This method is similar to traditional powder metallurgy method except that it employs microwave sintering. In microwave sintering, the heat is produced within the materials by microwaves, which radiates out after heating samples unlike in conventional sintering. To reduce the problem of variable heating the bi-directional hybrid microwave sintering was developed. Experimental setup (Gupta and Eugene, 2011) used for bi-directional hybrid microwave sintering is shown in Fig. 7. The SiC susceptors transmits the heat to billets from outside and microwaves absorbed by billets heats the billet from inside-out. This type of bi-directional heating ensures removal of thermal gradient, which automatically ensures a uniform heating of billets. The bi-directional microwave sintering technique assists in reducing sintering time and good integration between reinforcement and matrix. As the microwave sintering can be realized in relatively shorter period of time, undesirable reactions at the matrix/reinforcement interface can be minimized or prevented.

In disparity, in the view of conventional sintering a long sintering period is required that arise to non-beneficial reactions. Jayalakshmi *et al.* (2014) developed magnesium based metal matrix composites containing $\text{Ni}_{60}\text{Nb}_{40}$ metallic glass reinforcement particles using microwave sintering followed by extrusion.

Powder metallurgy accompanied with spark plasma sintering (SPS)

This method is similar to traditional powder metallurgy method except that it employs spark plasma sintering in place of conventional sintering. Spark plasma sintering (SPS) can be conducted in a short period of time and can ensure minimal grain growth. The simplified set up of the process (Zhang *et al.*, 2014) is presented in Fig. 8.

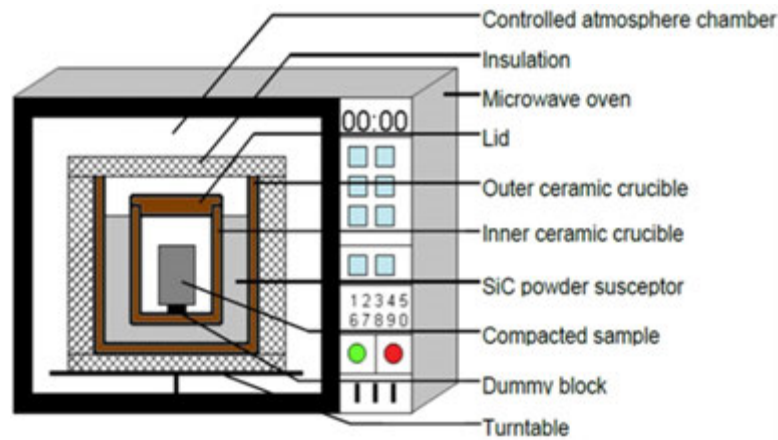


Fig. 7 Schematic setup for bi-directional hybrid microwave sintering.

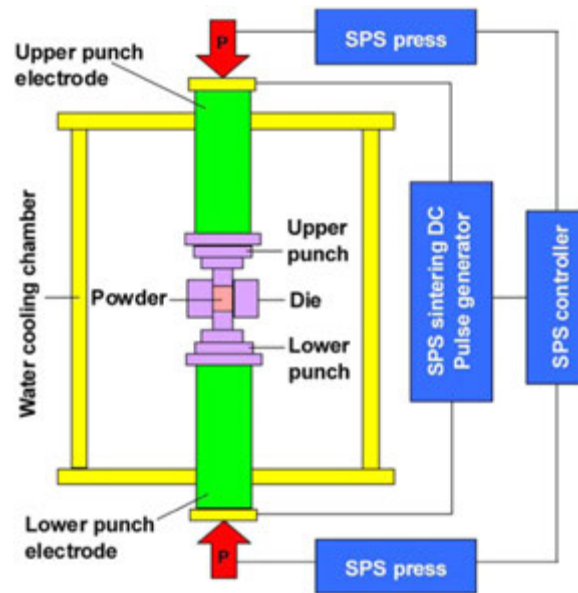


Fig. 8 Experimental setup for spark plasma sintering process.

In SPS sintering, the contribution of Joule heating effect in densification assists in compacting powders to near theoretical density. In SPS, the high heat rate (up to ~ 1000 K/min) which is generated internally is same as microwave sintering. $\text{Fe}_{50}\text{Cr}_{25}\text{Mo}_9\text{C}_{13}\text{B}_3$ metallic glass particles reinforced aluminum composites were successfully synthesized by spark plasma sintering assisted PM method (Guan *et al.*, 2020).

Powder metallurgy accompanied with high frequency induction heat sintering (HFIHS)

High frequency induction heat sintering (HFIHS) is a sintering technique in which metal and reinforcement are sintered rapidly (Khalil and Almajid, 2012). In order to heat the samples, an intense magnetic field is applied by an electrically conducting pressure die, during the operation of unit. Utilizing high temperature and pressure, the metallic powders can be quickly sintered in a short period of time. Grain growth does not occur in the sintered samples due to the high heating and cooling rates involved. Aljerf *et al.* (2012) produced $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{75}\text{B}_{20}\text{Si}_5]_{96}\text{Nb}_4$ metallic glassy particles reinforced Al composites by the HFIHS process.

Accumulative roll bonding (ARB)

Accumulative roll bonding (ARB) process to synthesize MMCs is shown in Fig. 9 (Saito *et al.*, 1999). ARB technique comprises of stacking of two sheets of same material with reinforcement particles in between the sheets (Ramanathan *et al.*, 2019).

The process is often repeated and heat treatment in between is normally involved. In ARB much emphasis is placed to clean the mating surfaces thoroughly to ensure good bonding between them. Choosing an appropriate temperature is one of the most

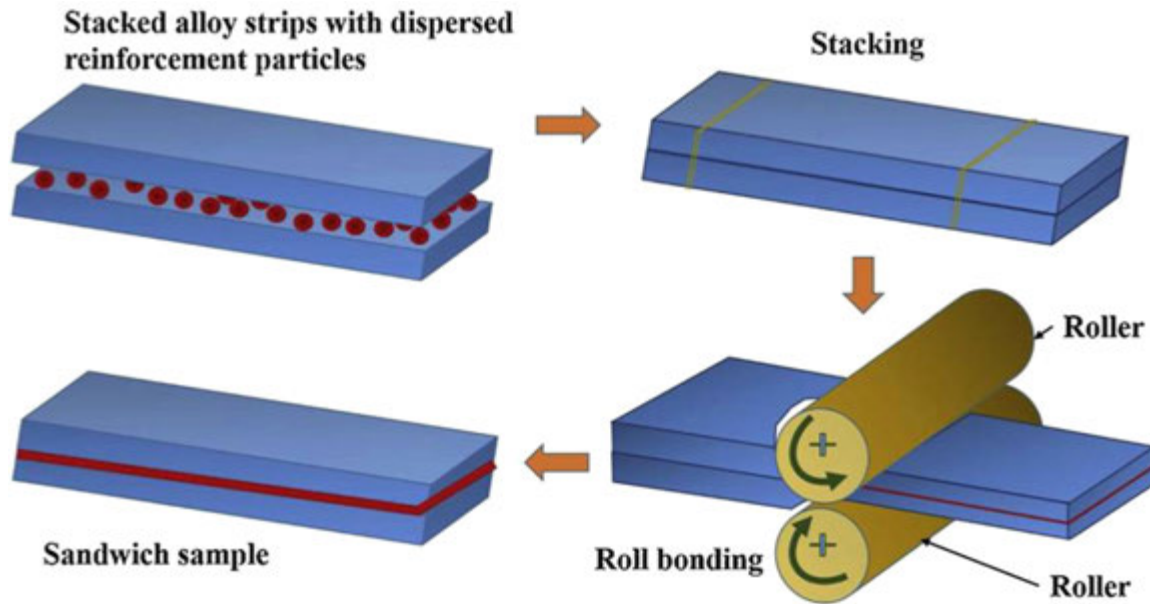


Fig. 9 Schematic of the ARB process.

important parameter in this technique. It should be less than recrystallization temperature of the amorphous reinforcement and at the same time should be able to ensure good bond strength between the sheets and particles. Khoramkhorshid *et al.* (2016) prepared $\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$ glassy particles reinforced Al composites by accumulative roll bonding (ARB) which exhibited excellent mechanical properties.

Friction stir processing (FSP)

Friction stir processing is an advanced version of friction stir welding, through which the surface composites can be fabricated conveniently (Wegłowski and Pietras, 2011). The rotating tool having shoulder and pin is kept in contact with the work piece continuously along the length and breadth of the surface. To fabricate a composite on metal surface, gaps are made which are filled with reinforcement powder later. A rapid plastic deformation and mixing of materials is obtained by the heat provided through friction generated when the FSP tool is passed through the gaps filled with reinforcement powders. An efficient enhancement was realized in the properties such as increased hardness, resistance to wear and corrosion fatigue in the materials that are modified by FSP. Magnesium matrix composites containing amorphous SiO_2 particles were fabricated through friction stir processing (Lee *et al.*, 2006).

Microstructure and Mechanical Properties of Al-based MMCs

Rezaei *et al.* (2016) produced aluminum based composites with $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ metallic glass reinforcement particles using equal channel angular pressing (ECAP) technique. In this process, mechanical alloying was used to prepare $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ metallic glass particles. In order to fabricate fully glass $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ particles, the ball milling was continuously repeated for 30 h. XRD patterns of the ball milled $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ glassy powder, pure Al and Al/AMG composites with varying reinforcement particles (5, 10 and 15 vol%) are shown in Fig. 10. The X-ray diffractogram of blended $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ powders showed a wide hump at $35^\circ \leq 2\theta \leq 50^\circ$, without the presence of any characteristic peaks representing an amorphous phase. Al/10vol% AMG composite exhibited 52% increase in yield strength when compared to pure Al.

Wang *et al.* (2014a) fabricated Al-based metallic glass ($\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$) particles reinforced Al matrix composites by powder metallurgy through hot pressing followed by hot extrusion. The authors reported that $\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$ reinforcement particles were distributed uniformly within the Al matrix with good metallurgical bonds. Also, they observed ~63% and 69% improvement in yield strength and ultimate tensile strength for the composite with 20 vol% of $\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$ reinforcement.

Balci *et al.* (2015) investigated 40 vol% of $\text{Fe}_{50.1}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.3}\text{Si}_{2.8}$ glassy particles reinforced Al composites processed through powder metallurgy and consolidation process. A detailed study of microstructure and mechanical properties was conducted. The SEM micrographs of extruded Al composites at different milling times are shown in Fig. 11. The hot extrusion was responsible for improvement in density and the absence of pores in SEM micrographs of the composite sample. The composite attained high strength (390 MPa) and remarkable plasticity (21%).

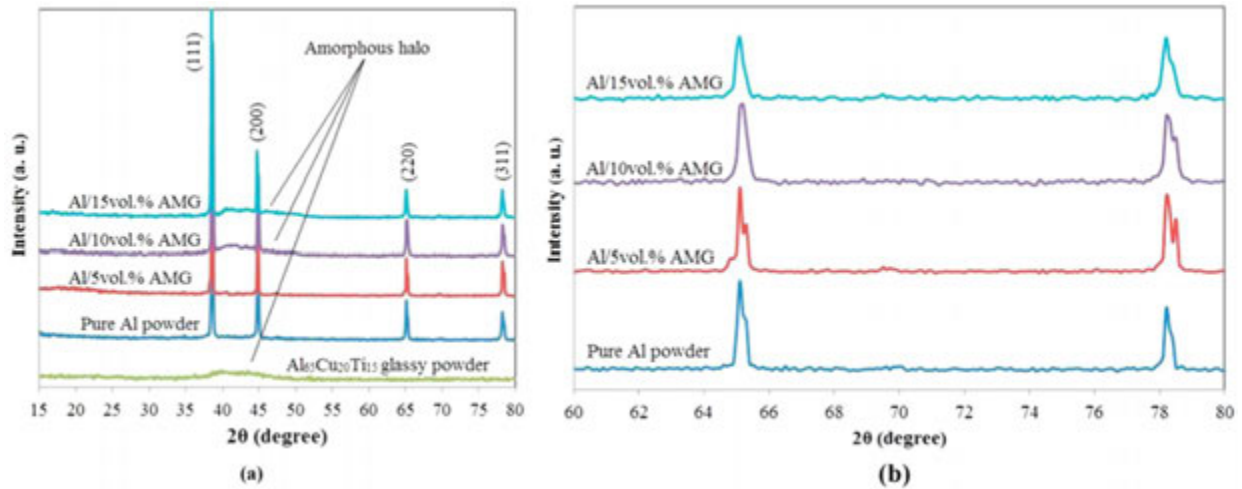


Fig. 10 (a) X-ray diffraction patterns of Al- $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ composites and (b) the enlarged figure showing broadening (220) and (311) peaks for the composites.

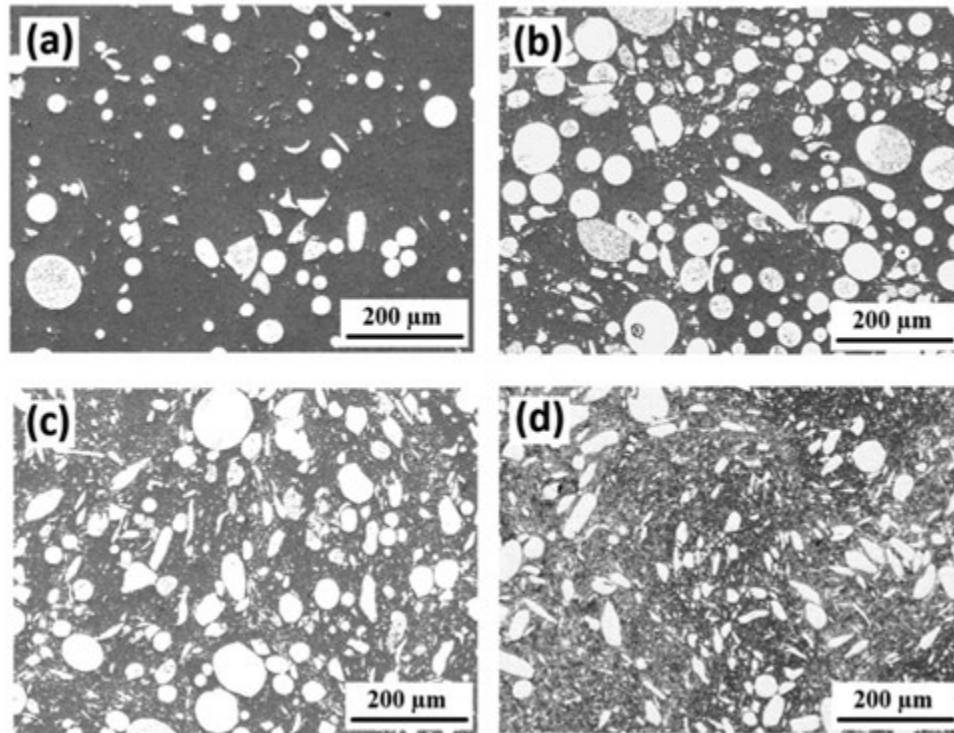


Fig. 11 SEM micrographs of Al-40 vol% $\text{Fe}_{50.1}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.3}\text{Si}_{2.8}$ composites at different milling times (a) 1 h, (b) 10 h, (c) 30 h and (d) 50 h.

Yuan *et al.* (2014) incorporated high volume percentage (40% and 60%) of Al-based ($\text{Al}_{60}\text{Cu}_{20}\text{Ti}_{15}\text{Zr}_5$) glassy alloy particles in pure Al matrix by using hot pressing method. In this investigation, Al-based ($\text{Al}_{60}\text{Cu}_{20}\text{Ti}_{15}\text{Zr}_5$) glassy alloy particles were successfully obtained after 120 h of ball milling.

The influence of the consolidation temperature on the structural and compression behavior of the composites was studied. At a temperature of 390°C , the densification values for 40 vol% Al and 60 vol% Al were found to be 91% and 96% respectively. They found that the Al-40 vol% $\text{Al}_{60}\text{Cu}_{20}\text{Ti}_{15}\text{Zr}_5$ composite consolidated at 390°C exhibited maximum yield strength and ultimate strength of 307 MPa and 353 MPa, respectively.

Guan *et al.* (2020) studied Al- $\text{Fe}_{50}\text{Cr}_{25}\text{Mo}_9\text{C}_{13}\text{B}_3$ composites developed using SPS technique and hot rolling method. They reported that shell structure had a unique effect on microstructure and compression behavior of the composites. The uniform

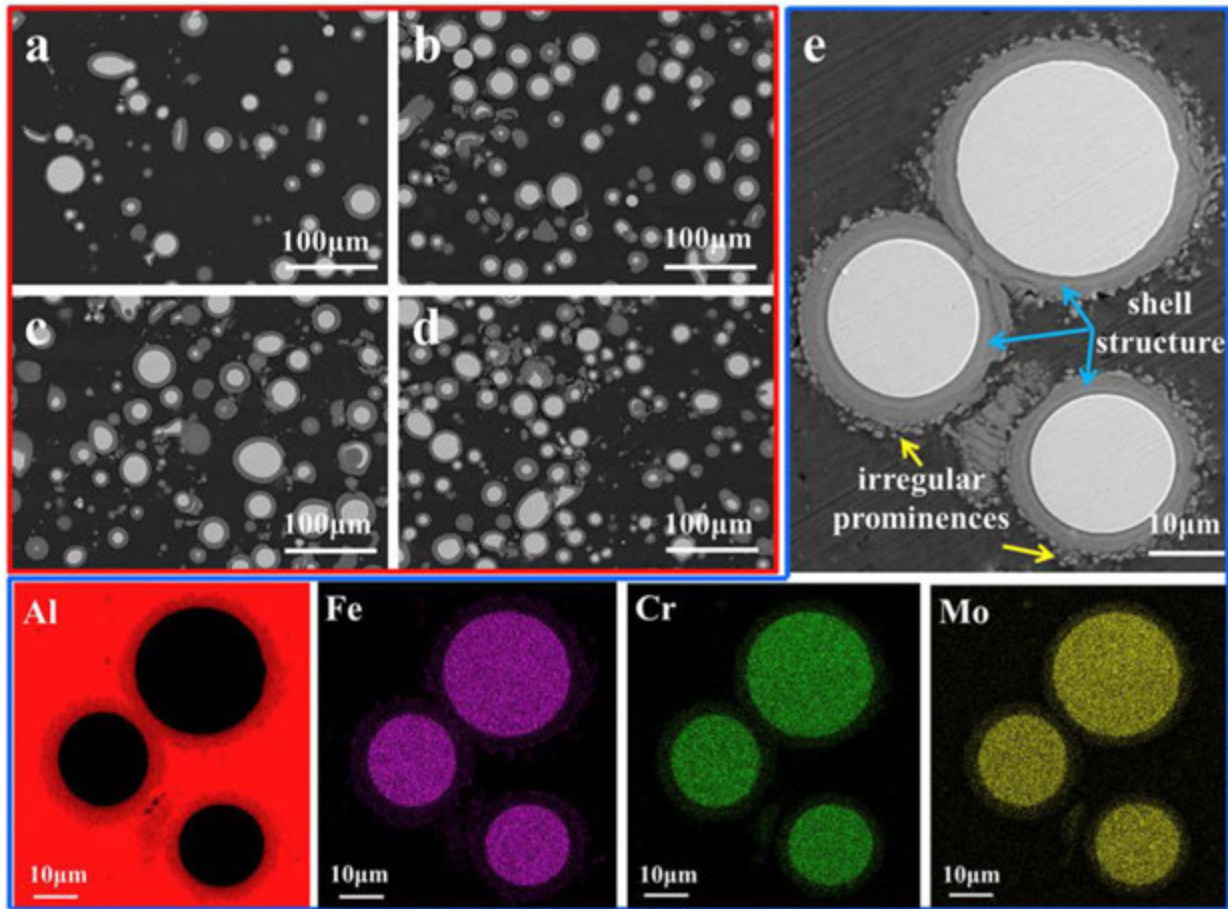


Fig. 12 (a)–(d) FESEM images of Al composites reinforced with FMG particles (10, 20, 30 and 40 vol%) and (e) higher magnification micrograph. The results of EDX mapping images (lower part) of the composite containing 40 vol% FMG particles.

distribution of the spherical Fe-based metallic glass FMG particles in the Al matrix is shown in **Fig. 12(a)–(d)**. **Fig. 12(e)** shows a high magnification micrograph of the composite containing 40 vol% of FMG particles.

The FMG particles resemble a concentric ring having a lot of uneven protrusions at the edge of the ring through which the surface of the FMG core was covered. The FMG core contained Fe, Cr and Mo.

[Jayalakshmi et al. \(2014\)](#) studied that the properties of the amorphous $\text{Ni}_{60}\text{Nb}_{40}$ alloy powders reinforced Al-based composites through bi-metallic microwave sintering technology which follows hot extrusion. The rapid improvement of mechanical properties of the Al- $\text{Ni}_{60}\text{Nb}_{40}$ composites has been attained by the amorphous reinforcement was concluded by the authors. When compared to pure Al, the compressive yield strength of the developed composite has increased from 40% to 100% with the increasing vol% of the reinforcement ($\text{Ni}_{60}\text{Nb}_{40}$).

[Zhang et al. \(2018\)](#) showed that CuZrAl metallic glass particles can be synthesized by mechanical alloying method. Sintering technique was employed to fabricate different volume fractions of CuZrAl particles reinforced Al-based composites. The microstructure and mechanical properties of the aluminum based composites were studied. The composite with 20 vol% CuZrAl reinforcement exhibited superior microhardness, yield strength and fracture strength of 290 HV, 408 MPa and 459 MPa, respectively. The enhancement in mechanical properties was attributed to the second phase strengthening, good interface, and grain refinement.

[Wang et al. \(2014b\)](#) developed $\text{Mg}_{58}\text{Cu}_{28.5}\text{Gd}_{11}\text{Ag}_{2.5}$ glassy particles reinforced Al matrix composites by powder metallurgy including hot pressing. They reported fairly uniform distribution of $\text{Mg}_{58}\text{Cu}_{28.5}\text{Gd}_{11}\text{Ag}_{2.5}$ glassy particles in the Al matrix. An enhancement in significant strength was reported primarily attributed to good reinforcement matrix interface.

[Zhou et al. \(2020\)](#) fabricated Al based composites containing $\text{Fe}_{52}\text{Cr}_{15}\text{Mo}_{26}\text{C}_3\text{B}_1\text{Y}_3$ amorphous particle using powder metallurgy technique. They reported the formation of near dense composites with uniform distribution of reinforcing particles. They reported tensile strength of 234 MPa for 20 vol% of Fe-metallic glass particles, which was 154% higher than that of pure Al. Besides, hardness was improved from 46 HV to 220 HV. The fracture mechanism of the composite was mostly mixed mode showing evidences of brittle and ductile fracture features.

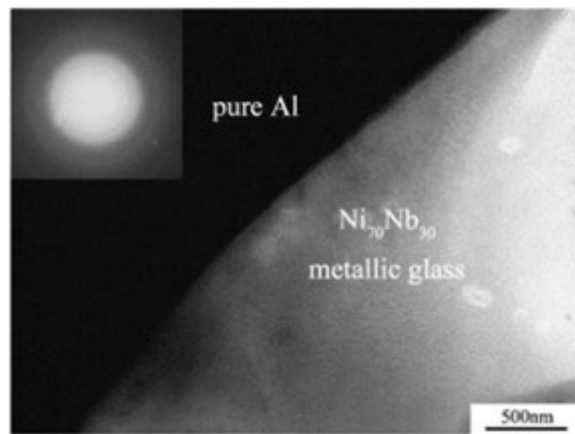


Fig. 13 TEM micrograph of Al-Ni₇₀Nb₃₀ composite.

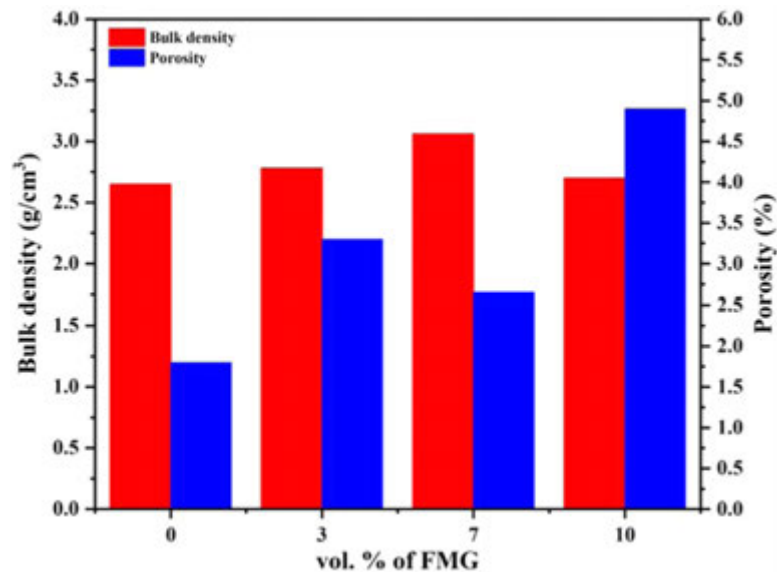


Fig. 14 The bulk density and porosity content of Al-Fe₅₂Cr₁₅Mo₂₆C₃B₁Y₃ composites.

Al-Ni₇₀Nb₃₀ amorphous composite through powder metallurgy technique was fabricated by [Yu et al. \(2006\)](#). The sintering temperature less than the melting point of Al (730 K) have been employed in the fabrication of the composite. [Fig. 13](#) represents the transmission electron microscopy (TEM) of the sintered sample, that explains a proper bond was formed in between Ni₇₀Nb₃₀ with the Al matrix, pore-free matrix and absence of any reaction zones.

[Rezaei et al. \(2020\)](#) prepared Fe-based metallic glass (FMG) reinforced novel Al composite through spark plasma sintering (SPS) method. The physical and mechanical characteristics of composite materials were investigated. They reported the retention of amorphous structure of the FMG reinforcement and absence of interfacial reactions in the consolidated Al-Fe₅₂Cr₁₅Mo₂₆C₃B₁Y₃ composites.

The difference in the bulk density and porosity of the composite samples is represented in [Fig. 14](#). The composite samples exhibited higher porosity when compared to pure Al. The bulk densities of all the samples were found to be almost equal irrespective of the presence of FMG particles.

To understand the magnitude of strength with addition of CNTs in Al, the tensile test results of CNT-reinforced pure Al and Al2024 are shown in [Fig. 12\(a\)](#) and [\(b\)](#), respectively.

[Zhang et al. \(2018\)](#) by using SPS phenomenon, Different amounts of (in vol%) of CuZrAl metallic amorphous particles have been reinforced into Al matrix. The mechanical properties of the SPSed composites have been noted. From [Fig. 15](#), It can be observed that with the increasing of vol% of CuZrAl, the microhardness of the composite have gradually enhanced. At 20 vol% of CuZrAl, the microhardness was found to be maximum enhancement, thereafter hardness showed a declining trend.

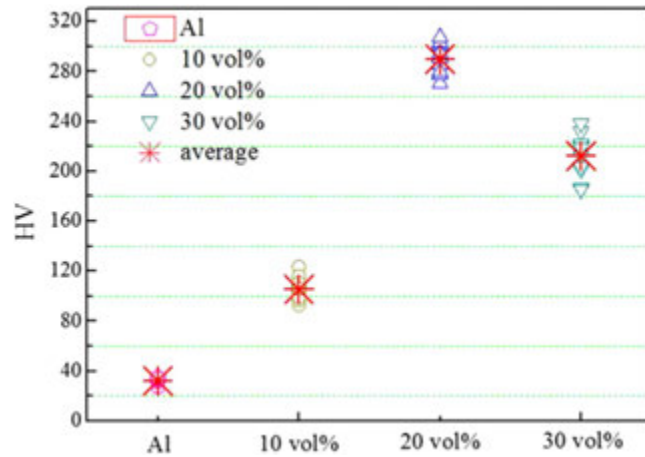


Fig. 15 Microhardness of the SPS processed pure Al and Al-CuZrAl composites.

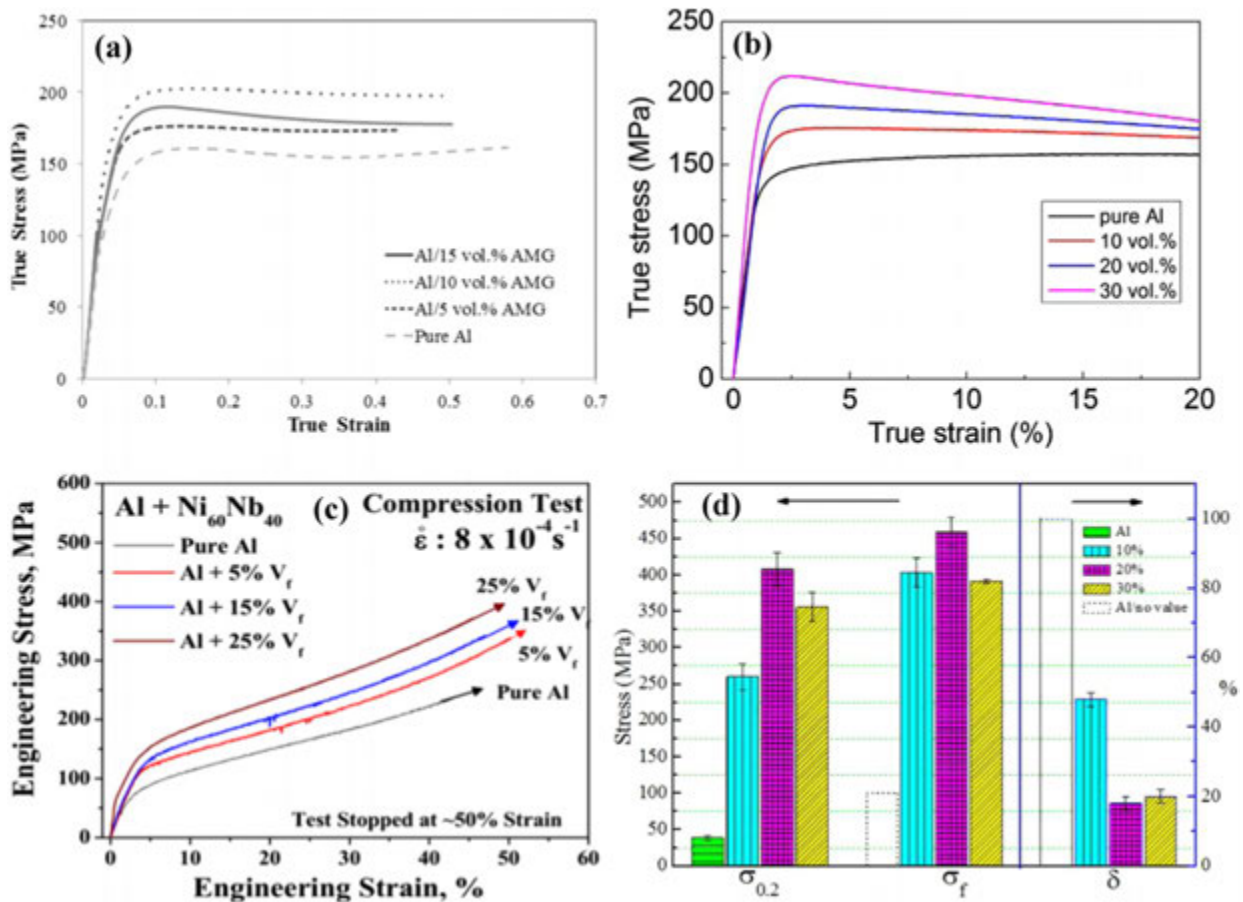


Fig. 16 True stress-true strain curves of (a) Al-Al₆₅Cu₂₀Ti₁₅ composites, (b) Al-Mg₅₈Cu_{28.5}Gd₁₁Ag_{2.5} composites, (c) Compression properties of Al-Ni₆₀Nb₄₀ composites, and (d) SPS-ed Al-CuZrAl composites.

To understand the magnitude of compressive strength with addition of amorphous particles in Al matrix, the compression test results of Al₆₅Cu₂₀Ti₁₅, Mg₅₈Cu_{28.5}Gd₁₁Ag_{2.5}, Ni₆₀Nb₄₀ and CuZrAl glassy particles reinforced Al based composites are shown in Fig. 16(a)–(d), respectively. The strength of the Al composites increases with the increasing amount of AMG reinforcement up to 10 vol% and hereafter a decrease in strength and ductility for Al/15 vol% AMG composite can be observed in Fig. 16(a). With the addition of glass reinforcement, the mechanical behavior of the Al matrix was enhanced significantly.

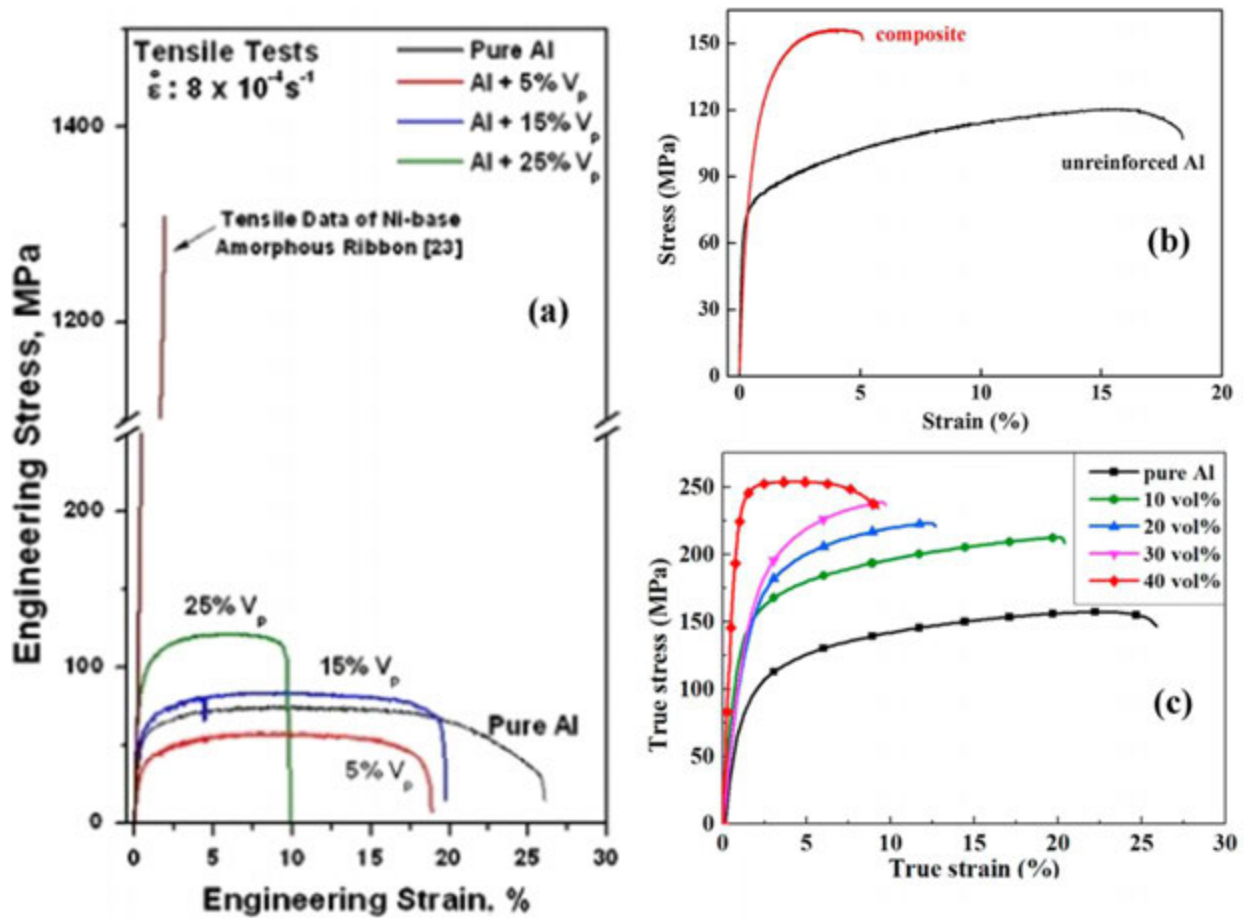


Fig. 17 Tensile properties of (a) Al-Ni₆₀Nb₄₀ composites, (b) Al-20 vol% Al₈₄Gd₆Ni₇Co₃ particles, and (c) tensile true stress-strain curves of the Al composites reinforced with Fe₅₀Cr₂₅Mo₉C₁₃B₃ metallic glass particles.

The strength of the Al composites increases with the increasing amount of AMG reinforcement up to 10vol% and hereafter a decrease in strength and ductility for Al/15 vol% AMG composite can be observed in Fig. 16(a). The compression stress-strain plots of Al-Mg₅₈Cu_{28.5}Gd₁₁Ag_{2.5} composite are presented in Fig. 16(b). With the addition of glass reinforcement, the mechanical behavior of the Al matrix was enhanced significantly. Considering 30 vol% glass-reinforced Al composite, the yield and compressive strength was improved by 38% and 35%, respectively. The representative stress-strain curves for hot extruded Al-Ni₆₀Nb₄₀ reinforced composites under compression loading are shown in Fig. 16(c). A significant enhancement in yield strength was realized due to the presence of amorphous reinforcement in the developed composites. The hot extruded composite showed about 45%–100% strength improvement with increase in volume fraction of Ni₆₀Nb₄₀ amorphous alloy particles. Compression property measurements of the SPS processed Al composites containing CuZrAl metallic glass particles are shown in Fig. 16(d). High yield strength ($\sigma_{0.2}$) and fracture strength (σ_f) was observed for spark plasma sintered Al-CuZrAl composites when compared to SPS processed pure Al. Al-20 vol% CuZrAl composites exhibited yield strength of 408 MPa which is improved by 946% when compared to pure Al (39 MPa). However, the compressive ductility of 20 vol% and 30 vol% of CuZrAl particles containing composites was marginally affected and stands at about 18% and 20%, respectively.

Fig. 17 shows the room temperature stress-strain curves for various amorphous particles reinforced Al composite samples under tensile loading. Fig. 17(a) shows the tensile stress-strain curves for the Al-Ni₆₀Nb₄₀ composites. The study revealed that a critical volume fraction (5%) of Ni₆₀Nb₄₀ reinforcement is required for improving the strength of aluminum. Ultimate tensile strength of Al-25vol% Ni₆₀Nb₄₀ composite was best and improved by ~60%. Fig. 17(b) shows a typical room temperature tensile stress-strain curve for the 20 vol% Al₈₄Gd₆Ni₇Co₃ particles reinforced Al matrix composite together with a curve for the unreinforced extruded pure Al. The yield strength and ultimate tensile strength of pure Al increased from 75 MPa and 93 MPa to 120 MPa and 157 MPa for Al-20 vol% due to the presence of Al₈₄Gd₆Ni₇Co₃ reinforcement. Room-temperature stress-strain curves of Al-Fe₅₀Cr₂₅Mo₉C₁₃B₃ composites are shown in Fig. 17(c). The ultimate tensile strength increases from 157 ± 6 MPa for pure Al to 212 ± 5 , 224 ± 4 , 239 ± 4 and 254 ± 5 MPa for the composites reinforced with 10, 20, 30 and 40 vol% FMG particles, respectively. For 40 vol% of FMG particles, there was an enhancement of about 60% in ultimate strength but the ductility was reduced to 9.3%. Ultimate tensile strength of Al-40 vol% Fe_{50.1}Co_{35.1}Nb_{7.7}B_{4.3}Si_{2.8} composite was found to be higher than

Table 1 Summary of research on Al metal matrix composites (Al-MMCs) containing amorphous reinforcing particles

Matrix + reinforcement	Processing techniques	Hardness (HV)	Compressive			Tensile			Reference
			YS (MPa)	UCS (MPa)	FS (%)	YS (MPa)	UTS (MPa)	EI (%)	
Al-15 vol% $\text{Fe}_{52}\text{Cr}_{15}\text{Mo}_{26}\text{C}_3\text{B}_1\text{Y}_3$	Powder Metallurgy (PM)	206	–	–	–	140	234	1.75	Zhou <i>et al.</i> (2020)
Al-30 wt% $\text{Ni}_{70}\text{Nb}_{30}$	Solid state process (PM)	–	111	146	>20	–	–	–	Yu <i>et al.</i> (2006)
Al-30 vol% $\text{Mg}_{58}\text{Cu}_{28.5}\text{Gd}_{11}\text{Ag}_{2.5}$	Hot pressing (PM)	–	180	212	>20	–	–	–	Wang <i>et al.</i> (2014b)
Al-5 vol% $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$	Equal channel angular pressing (ECAP) (PM)	–	168	172	0.50	–	–	–	Rezaei <i>et al.</i> (2016)
Al-10 vol% $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$		–	184	205	0.48	–	–	–	
Al-15 vol% $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$		–	153	182	0.42	–	–	–	
Al-20 vol% $\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$	Hot pressing + hot Extrusion (PM)	–	–	–	–	93	157	18	Wang <i>et al.</i> (2014a)
Al-40 vol% $\text{Fe}_{50.1}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.3}\text{Si}_{2.8}$	Hot pressing + hot Extrusion (PM)	144	–	–	–	340	470	6.5	Balci <i>et al.</i> (2015)
Al-40 vol% $\text{Al}_{60}\text{Cu}_{20}\text{Ti}_{15}\text{Zr}_5$	Hot pressing (PM)	–	–	–	–	307	353	5.8	Yuan <i>et al.</i> (2014)
Al + 5 vol% $\text{Ni}_{60}\text{Nb}_{40}$	Microwave sintering + Hot extrusion (PM)	74.5	114	300	>50	50	60	16.8	Jayalakshmi <i>et al.</i> (2013)
Al + 15 vol% $\text{Ni}_{60}\text{Nb}_{40}$		103.3	125	333	>50	75	85	18	
Al-25 vol% $\text{Ni}_{60}\text{Nb}_{40}$		125.2	155	375	>50	102	120	9.5	
Al-10 vol% $\text{Mg}_{65}\text{Cu}_{20}\text{Zn}_5\text{Y}_{10}$	Ball Milling + Hot Pressing (PM)	–	203	247	25	–	–	–	Wang <i>et al.</i> (2014c)
Al-30 vol% $\text{Mg}_{65}\text{Cu}_{20}\text{Zn}_5\text{Y}_{10}$		–	221	323	5.8	–	–	–	

the Al-40 vol% $\text{Fe}_{74}\text{Mo}_4\text{P}_{10}\text{C}_{7.5}\text{B}_{2.5}\text{Si}_{2.8}$ metallic glass composite (Zheng *et al.*, 2013). Al composite reinforced with core-shell structured FMG particles exhibited superior mechanical properties due the strong interfacial bonding (Miracle, 2005).

Table 1 summarizes the mechanical properties of Al matrix composites with various groups of amorphous reinforcement. It can be observed that Al-25 vol% $\text{Ni}_{60}\text{Nb}_{40}$ composite exhibited highest combination of yield strength and ultimate compressive strength at 155 MPa and 375 MPa, respectively. According to **Table 1**, the Al-40 vol% $\text{Fe}_{50.1}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.3}\text{Si}_{2.8}$ composite sample showed the maximum yield (340 MPa) and ultimate tensile strength (470 MPa). From the **Table 1** we can conclude that Fe-based glassy particles are one of the most potential replacements for the conventional ceramic or other metallic glass reinforcements.

Microstructure and Mechanical Properties of Mg-Based MMCs

In comparison to ceramic reinforcements, the metallic reinforcements have unique advantage of improving the interface compatibility with metal matrix. Jayalakshmi *et al.* (2014) developed Mg- $\text{Ni}_{60}\text{Nb}_{40}$ composites by PM method involving microwave sintering and hot extrusion. In this investigation, $\text{Ni}_{60}\text{Nb}_{40}$ (at%) amorphous alloy powder was prepared through mechanically alloying. XRD pattern of the ball milled $\text{Ni}_{60}\text{Nb}_{40}$ powder is shown in **Fig. 18(a)**. By successively ball milling of powders for 87 h, the amorphous characteristics in XRD studies were observed (a hump rather than sharp peaks). Thermal properties of the amorphous powders are shown in **Fig. 18(b)**. The onset and peak temperatures for crystallization $T_{x\text{-onset}}$ and $T_{x\text{-peak}}$ were observed at 605°C and 657°C, respectively. **Fig. 18(c)** represents FESEM image of $\text{Ni}_{60}\text{Nb}_{40}$ amorphous alloy powders with almost spherical morphology.

Fig. 19 shows the optical micrographs of extruded Mg- $\text{Ni}_{60}\text{Nb}_{40}$ composites. The values of the grain size obtained were found to be within the limits of the standard deviation which means the values are almost similar. When compared to pure Mg the matrix microstructure of all the composites possess fine grains. They concluded that the grain size was declined 2–3 times with respect to the pure Mg.

Sankaranarayanan *et al.* (2015b) fabricated $\text{Ni}_{50}\text{Ti}_{50}$ amorphous particles (3, 6 and 10 vol%) reinforced Mg-composites using microwave assisted rapid sintering and hot extrusion. Microstructural and mechanical behavior of the hot extruded composites were examined. XRD patterns of pure Mg and its composites are shown in **Fig. 20**. Prominent Mg-crystalline peaks and amorphous halo was observed in all the composites. To note that the amorphous halo at the diffraction angle $2\theta = 40^\circ$ was clearly observed in composite samples. By using microwave assisted powder metallurgy method, the novel glassy metallic particles can be incorporated into magnesium matrix successfully as confirmed by these observations. The distribution of $\text{Ni}_{50}\text{Ti}_{50}$ amorphous particles in the Mg matrix is presented in **Fig. 21(a)–(d)**. It reveals that the amorphous particles are distributed fairly uniformly in the matrix with good interface bonding.

Fig. 22(a) and **(b)** displays the ambient temperature stress–strain curves for the Mg- $\text{Ni}_{60}\text{Nb}_{40}$ and Mg- $\text{Ni}_{50}\text{Ti}_{50}$ composites under compression loading. From **Fig. 22(a)**, it can be observed that the strength of the composites increased due to the presence of

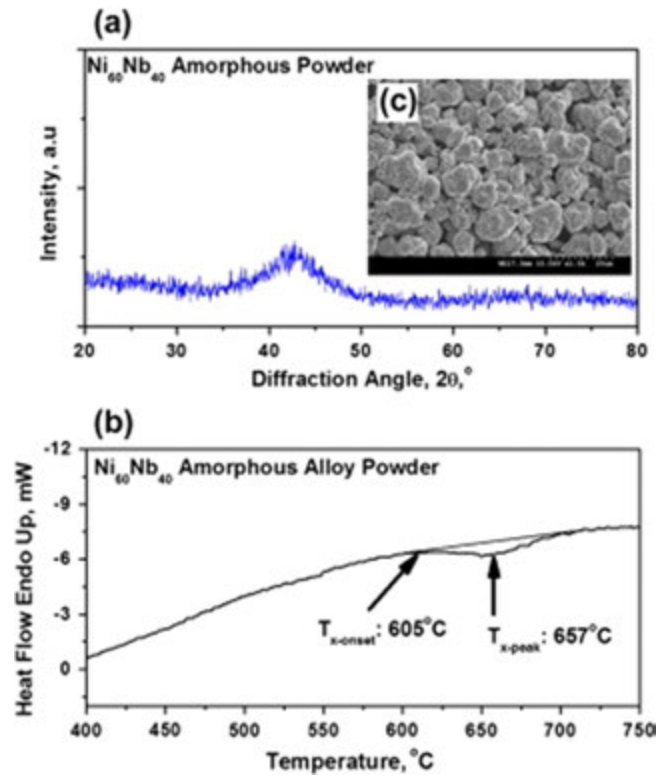


Fig. 18 (a) XRD pattern (b) DSC curve and (c) FESEM image of $\text{Ni}_{60}\text{Nb}_{40}$ amorphous alloy powder.

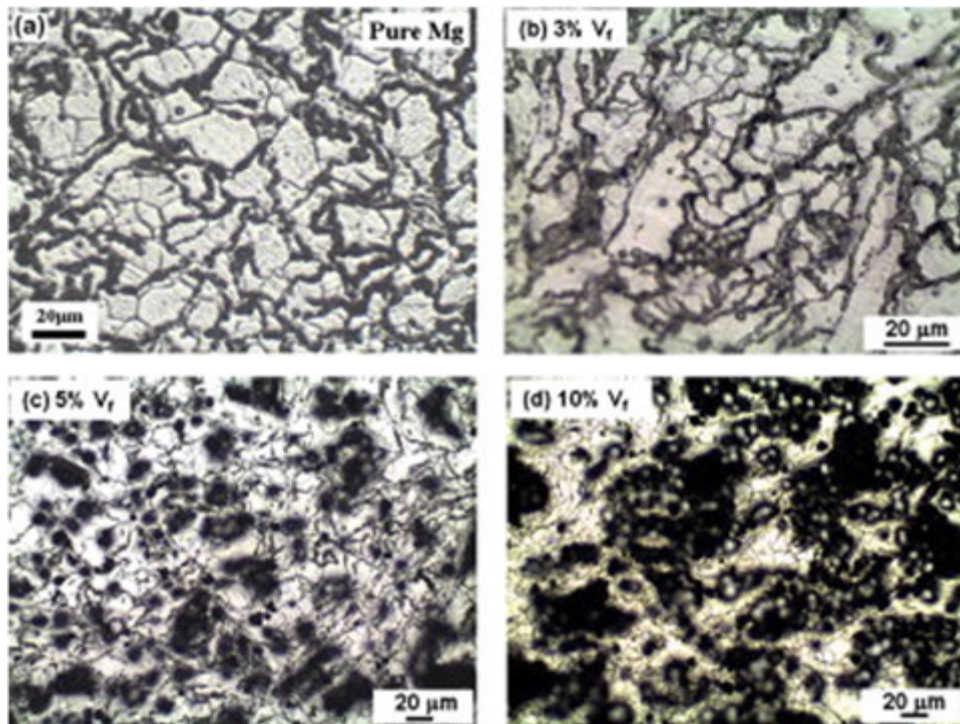


Fig. 19 (a)-(d) Optical micrographs of extruded $\text{Mg-Ni}_{60}\text{Nb}_{40}$ composites.

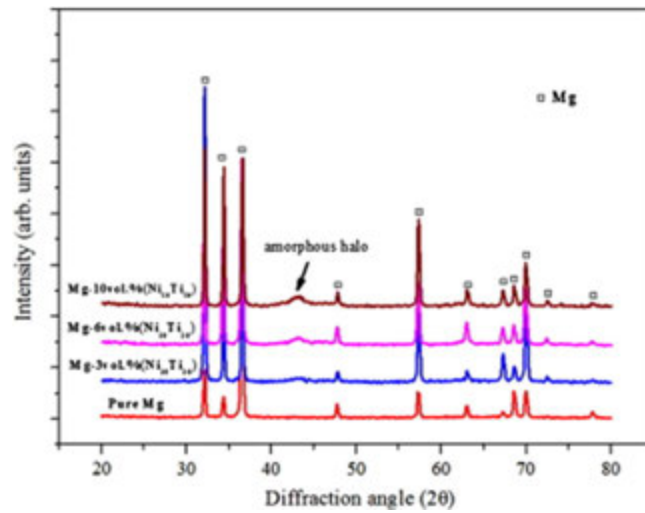


Fig. 20 X-ray diffractograms of the developed Mg-NiTi composites.

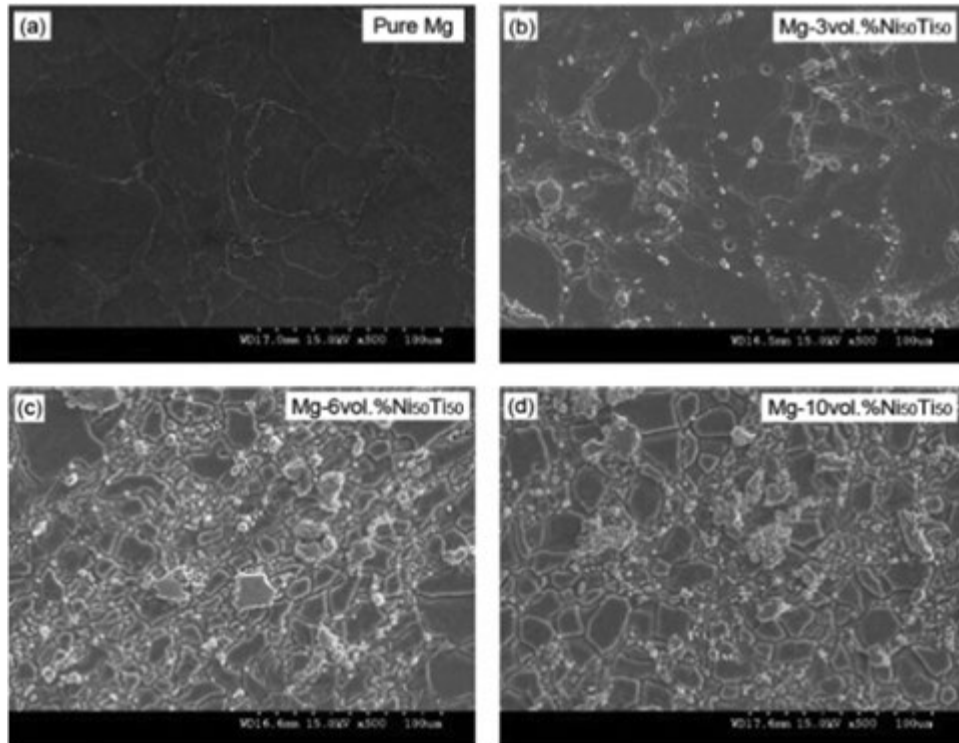


Fig. 21 (a)-(d) SEM micrographs of Mg-Ni₅₀Ti₅₀ composites.

Ni₆₀Nb₄₀. The compressive yield and ultimate strength of the Mg composite at 3 vol% increased by about ~20% where as at 5 vol% an improvement of about ~85% in yield strength and ~30% of ultimate strength was observed. The improvement in mechanical properties can be attributed the uniform distribution of Ni₆₀Nb₄₀ particles, Mg crystal orientation, effect of volume fraction and influence of amorphous reinforcements in matrix strengthening.

From the test results (**Fig. 22(b)**), the Ni₅₀Ti₅₀ amorphous particle reinforced Mg composites showed comparatively better improvement in both the compressive yield (CYS) and ultimate strength (UCS) with minimal variation in compressive ductility. For 3 vol% Ni₅₀Ti₅₀ particle addition, the CYS and UCS increased by ~15% and ~25%, respectively. For Mg-10 vol% Ni₅₀Ti₅₀ composite CYS and UCS increased by ~79% and ~71%, respectively. The results clearly validated that strengths of metallic matrix can be increased by the addition of amorphous Ni₅₀Ti₅₀ particles.

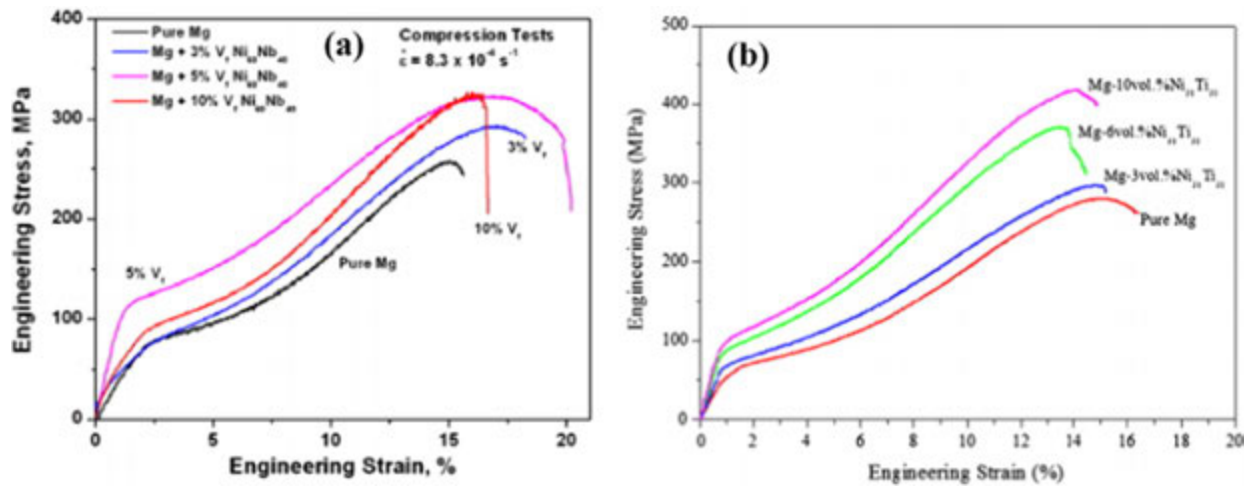


Fig. 22 Engineering stress–strain curves of (a) Mg–Ni₆₀Nb₄₀ and (b) Mg–Ni₅₀Ti₅₀ composites under compressive loading.

Table 2 Summary of research on Mg metal matrix composites (Mg–MMCs) reinforced by amorphous particles

Matrix + reinforcement	Processing techniques	Hardness (HV)	Compressive			Tensile			Reference
			YS (MPa)	UCS (MPa)	FS (%)	YS (MPa)	UTS (MPa)	EI (%)	
Mg-3 vol% Ni ₆₀ Nb ₄₀	Microwave Sintering + Hot Extrusion (PM)	62	85	283	17.6	–	–	–	Jayalakshmi <i>et al.</i> (2014)
Mg-5 vol% Ni ₆₀ Nb ₄₀		84	130	320	18.4	–	–	–	
Mg-10 vol% Ni ₆₀ Nb ₄₀		95	90	322	17.2	–	–	–	
Mg-3 vol% Ni ₅₀ Ti ₅₀	Microwave Sintering + Hot Extrusion (PM)	49	67	291	15.9	94	144	8.8	Sankaranarayanan <i>et al.</i> (2015b)
Mg-6 vol% Ni ₅₀ Ti ₅₀		62	89	368	15.1	127	183	6.5	
Mg-10 vol% Ni ₅₀ Ti ₅₀		66	102	417	14.9	148	178	2.0	
Mg-10 wt% Cu ₅₀ Ti ₅₀	Microwave Sintering + Hot Extrusion (PM)	63	93	403	17.5	–	–	–	Sankaranarayanan <i>et al.</i> (2015a)

Sankaranarayanan *et al.* (2015a) studied the copper-titanium based (Cu₅₀Ti₅₀) amorphous alloy particles reinforced Mg metal matrix using bi-directional microwave sintering process followed by hot extrusion. Authors reported that Cu₅₀Ti₅₀ amorphous alloy particles were distributed uniformly in Mg matrix without any interfacial reactions. The average hardness of the pure Mg was enhanced by ~25% with the addition of Cu₅₀Ti₅₀ amorphous reinforcement. The results of compressive properties of extruded pure Mg and Mg-10 wt% Cu₅₀Ti₅₀ composite are listed in Table 2. When compared to monolithic Mg, the yield and compressive strength of the Mg-10 wt% Cu₅₀Ti₅₀ composite improved by ~40% and ~45%, respectively. The results validated that addition of amorphous Cu₅₀Ti₅₀ particles enhanced strength properties of the Mg due to their high load bearing capacity (Gupta and Eugene, 2011).

Fig. 23 shows the room temperature tensile stress–strain curves of the extruded Mg–Ni₅₀Ti₅₀ composites. Significant improvement in tensile yield strength (TYS) and ultimate tensile strength (UTS) of Mg composites can be seen. The tensile yield and ultimate tensile strength increases from 75 MPa and 119 MPa to 148 MPa and 178 MPa for the Mg composite containing 10 vol% Ni₅₀Ti₅₀ particles. The developed Mg–10 vol% Ni₅₀Ti₅₀ composite exhibited an improvement of 98% in TYS and 50% in UTS, respectively. With the increasing volume percent of amorphous particle addition the tensile strength increased while ductility reduced progressively.

The research work reported in open literature reveals that the metallic glass reinforced Mg composites showed superior mechanical strength properties. The effects of processing method and volume fraction of amorphous reinforcements on the microhardness and strength (compressive/tensile strength) of the composites are presented in Table 2. From the table, it can be seen that the highest compression/tensile strength values are observed in Mg- 10 vol% Ni₅₀Ti₅₀ composite synthesized using microwave sintering followed by hot extrusion.

Current and Future Applications

In the aerospace and automotive industries, the reinforcements at micro/nano length scales in metallic matrices can lead to significant enhancement in properties. The applications of these materials can be targeted for small engines and electronic packing

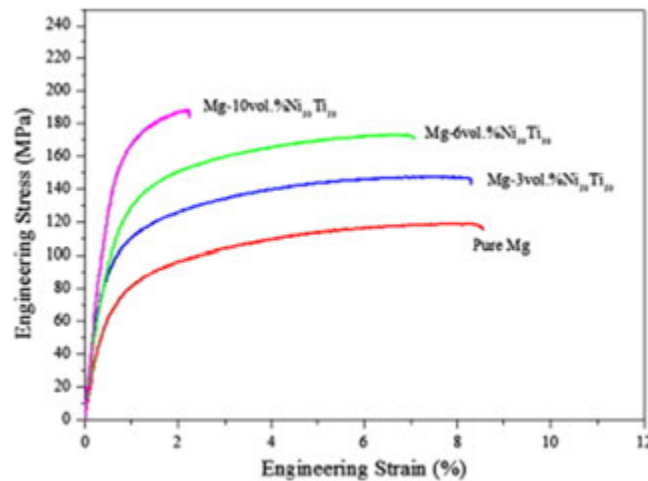


Fig. 23 Tensile engineering stress-strain curves for Mg-Ni₅₀Ti₅₀ composites.

applications as an example. The results have clearly validated that for metal matrix composites containing amorphous alloy particles, the strength of Al and Mg based composite can be clearly enhanced with comparatively much lower compromise in ductility (compared to ceramic reinforcements in micron length scale) which is required for strength based designs that traditionally follow bend-than-break philosophy. Further, the applicability of amorphous reinforcements in Al and Mg matrices makes them suitable candidates for weight critical applications such as in automotive, aerospace, space, electronics and defense industries. To note that amorphous alloy particles reinforced metal matrix composites can be designed to exhibit low density, high strength, high thermal conductivity and matching coefficient of thermal expansion, making them ideal candidate for such applications.

Summary

From the current understanding on composites containing amorphous particle reinforcement it can be concluded that various fabrication methods can be used for the manufacturing of such composites. Some of the key findings made on these composites are listed below.

- (1) Among the solid-based methods, bi-directional microwave sintering and spark plasma sintering appears to be the most promising techniques for the synthesis of MMCs with superior properties when compared to conventional methods.
- (2) Compared to ceramic reinforcement particles, Al-, Fe-, Ni-, Cu-, and Mg-based metallic glasses can be successfully employed to realize better mechanical properties particularly strength and hardness.
- (3) In improving the mechanical properties of the Al metal matrix containing Fe₅₀Cr₂₅Mo₉C₁₃B₃ metallic glass (FMG) particles, the core shell morphology plays a prominent role.
- (4) The Mg matrix grain size is decreased significantly and hardness is increased by the addition of Ni₅₀Ti₅₀ amorphous reinforcement.
- (5) The average hardness of 206 HV was observed for Al-15 vol% Fe₅₂Cr₁₅Mo₂₆C₃B₁Y₃ composite.
- (6) Al composites containing 25 vol% of Ni₆₀Nb₄₀ and 40 vol% of Fe_{50.1}Co_{35.1}Nb_{7.7}B_{4.3}Si_{2.8} amorphous reinforcement exhibited the highest ultimate compressive strength and ultimate tensile strength of 375 MPa and 470 MPa, respectively.
- (7) Mg composites containing 6 vol% and 10 vol% of Ni₅₀Ti₅₀ amorphous alloy particles exhibited the maximum ultimate tensile/compressive strength of 183 MPa and 417 MPa, respectively.
- (8) Amorphous particles reinforced metal matrix composites demonstrate good mechanical properties that are well suited to many industrial applications.

References

- Aljerf, M., Georgarakis, K., Louzguine-Luzgin, D., *et al.*, 2012. Strong and light metal matrix composites with metallic glass particulate reinforcement. *Materials Science and Engineering A*. doi:10.1016/j.msea.2011.10.098.
- Avedesian, M.M., Baker, H., 1999. *ASM Specialty Handbook: Magnesium and Magnesium Alloys*. Materials Park, OH: ASM International.
- Balci, Ö., Prashanth, K.G., Scudino, S., *et al.*, 2015. Effect of milling time and the consolidation process on the properties of Al matrix composites reinforced with Fe-based glassy particles. *Metals* 5, 669–685. doi:10.3390/met5020669.
- Dorward, R.C., Pritchett, T.R., 1988. Advanced aluminium alloys for aircraft and aerospace applications. *Materials and Design* 9 (2), 63–69. doi:10.1016/0261-3069(88)90076-3.
- Ekka, K.K., Chauhan, S.R., Varun, 2014. Dry sliding wear characteristics of SiC and Al₂O₃ nanoparticulate aluminium matrix composite using taguchi technique. *Arabian Journal for Science and Engineering* 40, 571–581. doi:10.1007/s13369-014-1528-2.

- El-Labban, H.F., Abdelaziz, M., Mahmoud, E.R.I., 2016. Preparation and characterization of squeeze cast-Al-Si piston alloy reinforced by Ni and nano-Al₂O₃ particles. *Journal of King Saud University - Engineering Sciences* 28, 230–239. doi:10.1016/j.jksues.2014.04.002.
- Gladston, J.A.K., Dinakaran, I., Sheriff, N.M., Selvam, J.D.R., 2017. Dry sliding wear behavior of AA6061 aluminum alloy composites reinforced rice husk ash particulates produced using copocasting. *Journal of Asian Ceramic Societies* 5 (2), 127–135. doi:10.1016/j.jascer.2017.03.005.
- Guan, H.D., Li, C.J., Gao, P., *et al.*, 2020. Aluminum matrix composites reinforced with metallic glass particles with core-shell structure. *Materials Science and Engineering A* 771, 138630. doi:10.1016/j.msea.2019.138630.
- Gupta, M., Eugene, W.W.L., 2011. *Microwaves and Metals*. Wiley. doi:10.1002/9780470822746.
- Gupta, M., Sharon, N.M.L., 2010. *Magnesium, Magnesium Alloys, and Magnesium Composites*. Wiley. doi:10.1002/9780470905098.
- Hwu, B.K., Lin, S.J., Jahn, M.T., 1996. The interfacial compounds and SEM fractography of squeeze-cast SiCp/6061 Al composites. *Materials Science and Engineering A* 206, 110–119. doi:10.1016/0921-5093(95)09979-4.
- Ibrahim, I.A., Mohamed, F.A., Lavernia, E.J., 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science* 26 (5), 1137–1156. doi:10.1007/BF00544448.
- Inoue, A., 2001. Bulk amorphous and nanocrystalline alloys with high functional properties. *Materials Science and Engineering A* 160. doi:10.1016/S0921-5093(00)01551-3.
- Jayalakshmi, S., Singh, R., Gupta, M., 2018. Metallic glasses as potential reinforcements in Al and Mg matrices: A review. *Technologies* 6 (40), 1–17. doi:10.3390/technologies6020040.
- Jayalakshmi, S., Gupta, S., Sankaranarayanan, S., Sahu, S., Gupta, M., 2013. Structural and mechanical properties of Ni60Nb40 amorphous alloy particle reinforced Al-based composites produced by microwave-assisted rapid sintering. *Materials Science and Engineering A* 581, 119–127. doi:10.1016/j.msea.2013.05.072.
- Jayalakshmi, S., Sahu, S., Sankaranarayanan, S., Gupta, S., Gupta, M., 2014. Development of novel Mg-Ni60Nb40 amorphous particle reinforced composites with enhanced hardness and compressive response. *Materials and Design* 53, 849–855. doi:10.1016/j.matdes.2013.07.022.
- Jayalakshmi, S., Gupta, M., 2015. *Metallic Amorphous Alloy Reinforcements in Light Metal Matrices*. Springer International Publishing. doi:10.1007/978-3-319-15016-1.
- Khalil, K.A., Almajid, A.A., 2012. Effect of high-frequency induction heat sintering conditions on the microstructure and mechanical properties of nanostructured magnesium/hydroxyapatite nanocomposites. *Materials and Design* 36, 58–68. doi:10.1016/j.matdes.2011.11.008.
- Khan, M.M., Nemati, A., Rahman, Z.U., *et al.*, 2018. Recent advancements in bulk metallic glasses and their applications: A review. *Critical Reviews in Solid State and Materials Sciences* 43 (3), 233–268. doi:10.1080/10408436.2017.1358149.
- Khoramkhorshid, S., Alizadeh, M., Taghvaei, A.H., Scudino, S., 2016. Microstructure and mechanical properties of Al-based metal matrix composites reinforced with Al₈₄Gd₆Ni₇Co₃ glassy particles produced by accumulative roll bonding. *Materials and Design* 90 (15), 137–144. doi:10.1016/j.matdes.2015.10.063.
- Lee, C.J., Huang, J.C., Hsieh, P.J., 2006. Mg based nano-composites fabricated by friction stir processing. *Scripta Materialia* 54 (7), 1415–1420. doi:10.1016/j.scriptamat.2005.11.056.
- Lee, M.H., Kim, J.H., Park, J.S., *et al.*, 2004. Fabrication of Ni-Nb-Ta metallic glass reinforced Al-based alloy matrix composites by infiltration casting process. *Scripta Materialia* 50, 1367–1371. doi:10.1016/j.scriptamat.2004.02.038.
- Matli, P.R., Manakari, V., Parande, G., *et al.*, 2020. Improving mechanical, thermal and damping properties of NiTi (Nitinol) reinforced aluminum nanocomposites. *Journal of Composites Science* 4 (1), 19. doi:10.3390/jcs4010019.
- Meenashisundaram, G.K., Nai, M.H., Almajid, A., Gupta, M., 2015. Development of high performance Mg-TiO₂ nanocomposites targeting for biomedical/structural applications. *Materials and Design* 65, 104–114. doi:10.1016/j.matdes.2014.08.041.
- Miracle, D.B., 2005. Metal matrix composites – From science to technological significance. *Composites Science and Technology* 65, 2526–2540. doi:10.1016/j.compscitech.2005.05.027.
- Prabu, S.B., Karunamoorthy, L., Kathiresan, S., Mohan, B., 2006. Influence of stirring speed and stirring time on distribution of particles in cast metal matrix composite. *Journal of Materials Processing Technology* 171 (2), 268–273. doi:10.1016/j.jmatprotec.2005.06.071.
- Rajak, D.K., Pagar, D.D., Kumar, R., Pruncu, C.I., 2019. Recent progress of reinforcement materials: A comprehensive overview of composite materials. *Journal of Materials Research and Technology* 8 (6), 6354–6374. doi:10.1016/j.jmrt.2019.09.068.
- Rajan, T.P.D., Pillai, R.M., Pai, B.C., 1998. Reinforcement coatings and interfaces in aluminium metal matrix composites. *Journal of Materials Science* 33, 3491–3503. doi:10.1023/A:1004674822751.
- Ramanathan, A., Krishnan, P.K., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *Journal of Manufacturing Processes* 42, 213–245. doi:10.1016/j.jmapro.2019.04.017.
- Rawal, S., 2001. Metal-matrix composites for space applications. *JOM* 53, 14–17. doi:10.1007/s11837-001-0139-z.
- Reddy, M.P., Shakoar, R.A., Parande, G., *et al.*, 2017a. Enhanced performance of nano-sized SiC reinforced Al metal matrix nanocomposites synthesized through microwave sintering and hot extrusion techniques. *Progress in Natural Science: Materials International* 27 (5), 606–614. doi:10.1016/j.pnsc.2017.08.015.
- Reddy, M.P., Ubaid, F., Shakoar, R.A., *et al.*, 2017b. Effect of reinforcement concentration on the properties of hot extruded Al-Al₂O₃ composites synthesized through microwave sintering process. *Materials Science and Engineering A* 696 (April), 60–69. doi:10.1016/j.msea.2017.04.064.
- Reddy, M.P., Manakari, V., Parande, G., *et al.*, 2019. Structural, mechanical and thermal characteristics of Al-Cu-Li particle reinforced Al-matrix composites synthesized by microwave sintering and hot extrusion. *Composites Part B: Engineering* 164, 485–492. doi:10.1016/j.compositesb.2019.01.063.
- Rezaei, M.R., Razzavi, S.H., Shabestari, S.G., 2016. Development of a novel Al-Cu-Ti metallic glass reinforced Al matrix composite consolidated through equal channel angular pressing (ECAP). *Journal of Alloys and Compounds* 673, 17–27. doi:10.1016/j.jallcom.2016.02.234.
- Rezaei, M.R., Albooyeh, A., Shayestefar, M., Shiraghaei, H., 2020. Microstructural and mechanical properties of a novel Al-based hybrid composite reinforced with metallic glass and ceramic particles. *Materials Science and Engineering A* 786, 139440. doi:10.1016/j.msea.2020.139440.
- Safri, S.N.A., Sultan, M.T.H., Jawaid, M., Jayakrishna, K., 2018. Impact behaviour of hybrid composites for structural applications: A review. *Composites Part B: Engineering* 133, 112–121. doi:10.1016/j.compositesb.2017.09.008.
- Saito, Y., Utsunomiya, H., Tsuji, N., Sakai, T., 1999. Novel ultra-high straining process for bulk materials development of the accumulative roll-bonding (ARB) process. *Acta Materialia* 47, 579–583. doi:10.1016/S1359-6454(98)00365-6.
- Sankaranarayanan, S., Agrawal, N., Jayalakshmi, S., Nguyen, Q.B., Gupta, M., 2015a. Synthesis and characterization of novel magnesium materials containing copper-titanium based (Cu₅₀Ti₅₀) amorphous alloy particles. *Magnesium Technology* 627, 192–199. doi:10.1002/9781119093428.ch72.
- Sankaranarayanan, S., Hemanth Shankar, V., Jayalakshmi, S., Quy Bau, N., Gupta, M., 2015b. Development of high performance magnesium composites using Ni₅₀Ti₅₀ metallic glass reinforcement and microwave sintering approach. *Journal of Alloys and Compounds*, 387–390. doi:10.1016/j.jallcom.2014.12.009.
- Scudino, S., Surreddi, K.B., Sager, S., *et al.*, 2008. Production and mechanical properties of metallic glass-reinforced Al-based metal matrix composites. *Journal of Materials Science*. doi:10.1007/s10853-008-2647-5.
- Scudino, S., Liu, G., Prashanth, K.G., *et al.*, 2009. Mechanical properties of Al-based metal matrix composites reinforced with Zr-based glassy particles produced by powder metallurgy. *Acta Materialia*. doi:10.1016/j.actamat.2009.01.010.
- Surappa, M.K., 2003. Aluminium matrix composites: Challenges and opportunities. *Sadhana - Academy Proceedings in Engineering Sciences* 28 (1–2), 319–334. doi:10.1007/BF02717141.
- Suryanarayana, C., 2001. Mechanical alloying and milling. In: Arzt, E., Salieb-Beugelaar, G. (Eds.), *Progress in Materials Science*, vol. 46. Elsevier, pp. 1–184. doi:10.1016/S0079-6425(99)00010-9.
- Ubaid, F., Matli, P.R., Shakoar, R.A., *et al.*, 2017. Using B4C nanoparticles to enhance thermal and mechanical response of aluminum. *Materials* 10 (6), 2–13. doi:10.3390/ma10060621.

- Wang, Z., Prashanth, K.G., Scudino, S., *et al.*, 2014a. Tensile properties of Al matrix composites reinforced with in situ devitrified Al₈₄Gd₆Ni₇Co₃ glassy particles. *Journal of Alloys and Compounds* 586, S419–S422. doi:10.1016/j.jallcom.2013.04.190.
- Wang, Z., Tan, J., Scudino, S., *et al.*, 2014b. Mechanical behavior of Al-based matrix composites reinforced with Mg₅₈Cu_{28.5}Gd₁₁Ag_{2.5} metallic glasses. *Advanced Powder Technology* 25, 635–639. doi:10.1016/j.appt.2013.10.005.
- Wang, Z., Tan, J., Sun, B.A., *et al.*, 2014c. Fabrication and mechanical properties of Al-based metal matrix composites reinforced with Mg₆₅Cu₂₀Zn₅Y₁₀ metallic glass particles. *Materials Science and Engineering A* 600, 53–58. doi:10.1016/j.msea.2014.02.003.
- Weglowski, M.S.T., Pietras, A., 2011. Friction stir processing – Analysis of the process. *Archives of Metallurgy and Materials* 56, 779–788. doi:10.2478/v10172-011-0086-9.
- Xiang, S., Wang, X., Gupta, M., *et al.*, 2016. Graphene nanoplatelets induced heterogeneous bimodal structural magnesium matrix composites with enhanced mechanical properties. *Scientific Reports* 6, 38824. doi:10.1038/srep38824.
- Yu, P., Kim, K.B., Das, J., *et al.*, 2006. Fabrication and mechanical properties of Ni-Nb metallic glass particle-reinforced Al-based metal matrix composite. *Scripta Materialia* 54 (8), 1445–1450. doi:10.1016/j.scriptamat.2006.01.001.
- Yuan, M., Zhang, D.C., Tan, C.G., *et al.*, 2014. Microstructure and properties of Al-based metal matrix composites reinforced by Al₆₀Cu₂₀Ti₁₅Zr₅ glassy particles by high pressure hot pressing consolidation. *Materials Science and Engineering A* 590, 301–306. doi:10.1016/j.msea.2013.10.049.
- Zhang, L., Li, B., Wu, H., *et al.*, 2018. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Advanced Powder Technology* 29, 1695–1702. doi:10.1016/j.appt.2018.04.004.
- Zhang, Z.H., Liu, Z.F., Lu, J.F., *et al.*, 2014. The sintering mechanism in spark plasma sintering – Proof of the occurrence of spark discharge. *Scripta Materialia* 25, 635–639. doi:10.1016/j.scriptamat.2014.03.011.
- Zheng, R., Hao, X., Yuan, Y., *et al.*, 2013. Effect of high volume fraction of B₄C particles on the microstructure and mechanical properties of aluminum alloy based composites. *Journal of Alloys and Compounds* 576, 291–298. doi:10.1016/j.jallcom.2013.04.141.
- Zhou, X., Long, W., Zhou, X., 2020. Study on microstructure and mechanical properties of Fe-based amorphous particle-reinforced Al-based matrix composites. *Advanced Composites Letters* 29, 1–10. doi:10.1177/2633366 × 20921402.

Development and Properties of Amorphous Particles Reinforced Al Matrix Nanocomposites

Adnan Khan and Mattli M Reddy, Qatar University, Doha, Qatar

Penchal Reddy Matli, National University of Singapore, Singapore

Rana A Shakoor, Qatar University, Doha, Qatar

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Development of lightweight materials is of great interest for weight-sensitive applications such as automotive, defense and aerospace industries. Light metals offer high specific strength properties and thus provide energy and fuel efficiency. Amongst the existing light metals such as titanium (Ti), aluminum (Al) and magnesium (Mg), aluminum (Al) is attractive due to its low density, high ductility, malleability, good conductivity, high specific strength and its abundant availability (8% of earth crust is aluminum). Aluminum can be reinforced with suitable reinforcement to improve its properties such as high strength to weight ratio, low coefficients of thermal expansion, good wear properties, excellent corrosion resistance and good ductility when compared to the conventional aluminum alloys. Aluminum metal matrix composites are increasingly being used for car parts that are exposed to high loads, such as e.g., piston, brake disks, engine cylinders, drum brakes, push rods, cam gears and others (Babalola *et al.*, 2014; El-Labban *et al.*, 2014; Jiang *et al.*, 2014; Wahyuni *et al.*, 2019).

The tempting properties of Al-based composites make them attractive for a wide variety of commercial/industrial applications (Hatch, 1984; Polmear, 1995). Despite the fact, that Al-based composites have attractive properties, however, their structural, thermal-mechanical, and electrical properties are essentially required to be further modified to address the more demanding future challenges and applications. Usually, Al metal matrix composites (AMMCs) are fabricated by the incorporation of stronger/stiffer and thermally stable non-metallic/ceramic reinforcements (Al_2O_3 , SiC, TiC BN, AlN etc.) into the aluminum matrix to achieve enhanced performance (Pradhan *et al.*, 2015; Reddy *et al.*, 2017a,b; Reddy *et al.*, 2018a,b). The salient features of AMMCs when compared to Al alloys are short-listed below (Surappa, 2003; Stojanović and Ivanović 2015):

- Higher stiffness and strength
- Lower density (weight)
- Controllable thermal properties (heat control/management)
- Improved vibration damping capability
- Enhanced mechanical properties
- Improved stiffness
- Great strength
- Enhanced electrical performance
- Improved abrasion and wear resistance
- Improved high temperature properties

Given the fact that AMMCs can provide superior performance in contrast to their unreinforced alloys, they have found their role as structural and functional materials in advanced applications such as electronic packaging and space/aerospace industries, in addition to being well-utilized in automotive industries, military armory and sporting goods. The current and prospective applications of AMMCs in various commercial/industrial sectors have been shown in Fig. 1 (Lloyd, 1994; Rawal, 2001; Miracle, 2005).

The major limitation of AMMCs in expending their utilization is their low ductility, which is due to the poor interfacial characteristics. This occurs because of the low wettability between the matrix and the reinforcement particles. As a promising solution to overcome the existing limitation (i.e., low ductility) of AMMCs (with conventional ceramic reinforcements), we propose to employ a new class of reinforcements, namely metallic amorphous alloys (AAs)/bulk metallic glasses (BMGs), as a better alternative for the conventional reinforcements. Amorphous metallic alloys or metallic glasses are relative newcomers to the world of glasses, and they have properties that are unusual for metallic solids. Metallic glasses, which exist in a very wide variety of compositions, combine fundamental interest with practical applications. In order to understand the concept of amorphous metallic alloys let us consider Fig. 2 in which crystalline and amorphous structures are presented. In a crystal (below left), there is a great deal of regularity or order to the atomic positions. In comparison, the atomic positions in a glass (below right) are much more disordered. In the crystal, the local environment around each atom is the same, whereas, in the glass, each atom has about six neighbors on average, but some atoms have fewer than six while others have more.

From the last two decades, metallic amorphous alloys (AAs)/bulk metallic glasses (BMGs) are a new class of materials that inherently have superior mechanical properties. This is because of the fact that these are distinctly different from conventional metals in terms of their structure (i.e., the sense of long-range atomic order), metastable thermal behavior (i.e., the presence of glass transition temperature (T_g)), and crystallization temperature (T_x) as shown in Figs. 3 and 4.

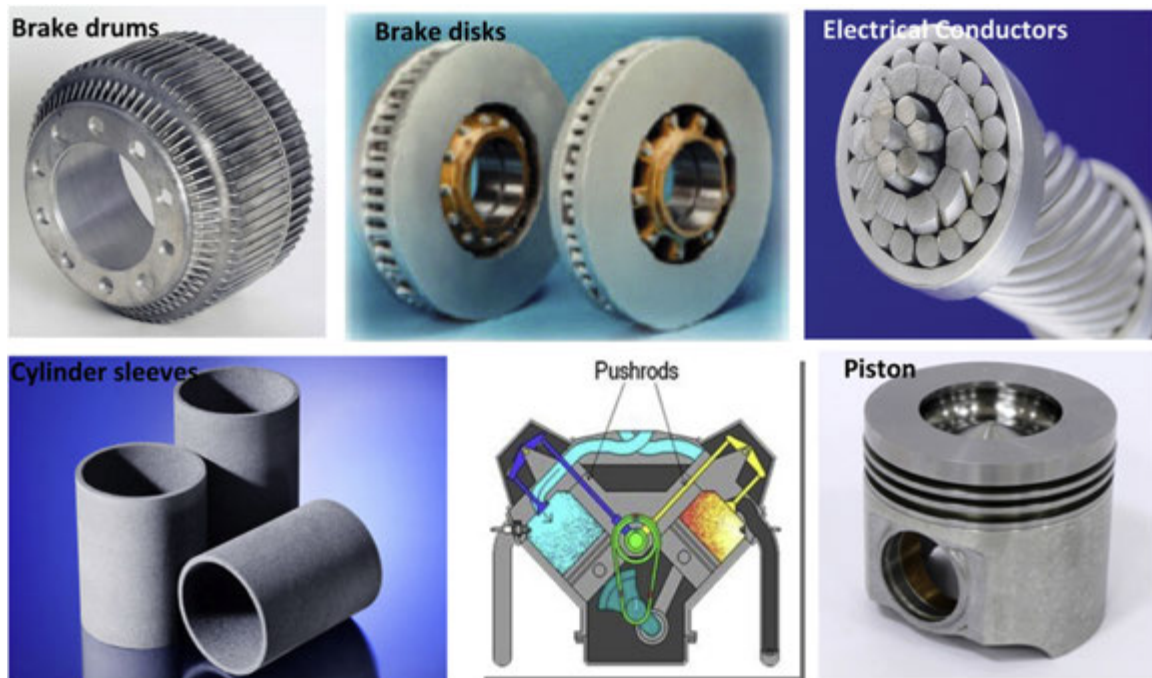


Fig. 1 Some industrial aluminum metal matrix composites.

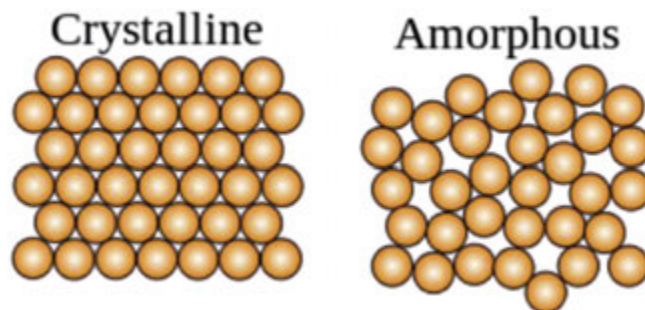


Fig. 2 Different degrees of ordered structures: crystal (left) and amorphous (right). Reproduced from Zallen, R., 2008. The physics of amorphous solids. John Wiley & Sons.

With this unique structure, amorphous alloys exhibit high strength ($\sim 1\text{--}2$ GPa), large elastic strain limit ($\sim 1\%\text{--}2\%$) and high corrosion resistance when compared to the conventional materials (Luborsky, 1983; Telford, 2004; Sheng *et al.*, 2006; Dąbrowa *et al.*, 2015; Jayalakshmi and Gupta, 2015). Moreover, due to their high strain limit and high strength, metallic glass is a natural candidate for use as a reinforcement in composite materials.

There have been a large number of attempts to develop composites with amorphous reinforcements. Issa *et al.* (2017) reported the fabrication and mechanical properties of aluminum/amorphous SiO_2 nanocomposites with different weight percent of SiO_2 (0–3.0 wt%) using powder metallurgy and hot extrusion techniques. The SiO_2 nanoparticles were not visible in the micrographs because of their small size and low in content. It is reported that the addition of 1.0 wt% amorphous silica nanoparticle to Al, has resulted in the improvement of tensile strength and hardness by $\sim 25\%$ and 42% respectively. Jayalakshmi *et al.* (2013) made an attempt to improve the mechanical strength of pure aluminum by the presence of $\text{Ni}_{60}\text{Nb}_{40}$ amorphous alloy powder. $\text{Ni}_{60}\text{Nb}_{40}$ (5, 15 and 25 vol%) was reinforced into aluminum matrix, and the composites were prepared using a novel microwave-assisted rapid sintering technique, followed by a hot extrusion process. It is reported that the hardness and compressive strength values increase with an increasing amount of $\text{Ni}_{60}\text{Nb}_{40}$ reinforcement. The highest concentration of reinforcement (25%) resulted in a significant increase in strength ($\sim 60\%$) due to efficient load transfer and matrix strengthening phenomenon. Lee *et al.* (2004) reported the fabrication and mechanical properties of Ni-Nb-Ta (Ni–20.6 Nb–40.2Ta) amorphous alloy ribbons reinforced aluminum composites prepared by the infiltration casting process. It is reported that the Ni–20.6 Nb–40.2Ta metallic glass ribbons were uniformly distributed in the Al matrix. It was observed that the addition of Ni–20.6 Nb–40.2Ta (wt%) as reinforcements to

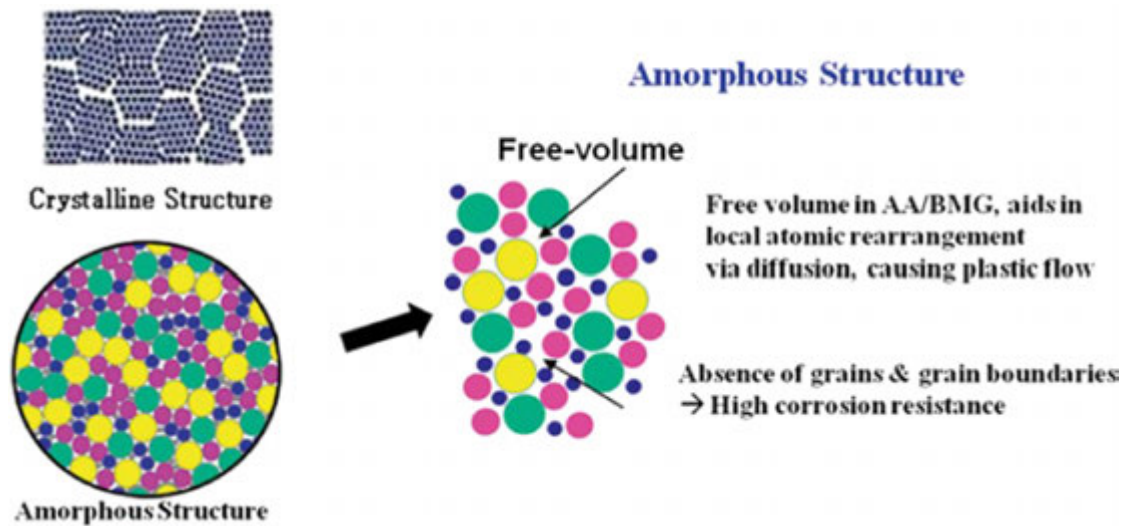


Fig. 3 Schematic showing the presence of free volume in the amorphous structure. Reproduced from Jayalakshmi, S., Gupta, M., 2015. Light metal matrix composites with amorphous alloys/bulk metallic glass reinforcements (BMG). In: *Metallic Amorphous Alloy Reinforcements in Light Metal Matrices*. Springer, pp. 85–106.

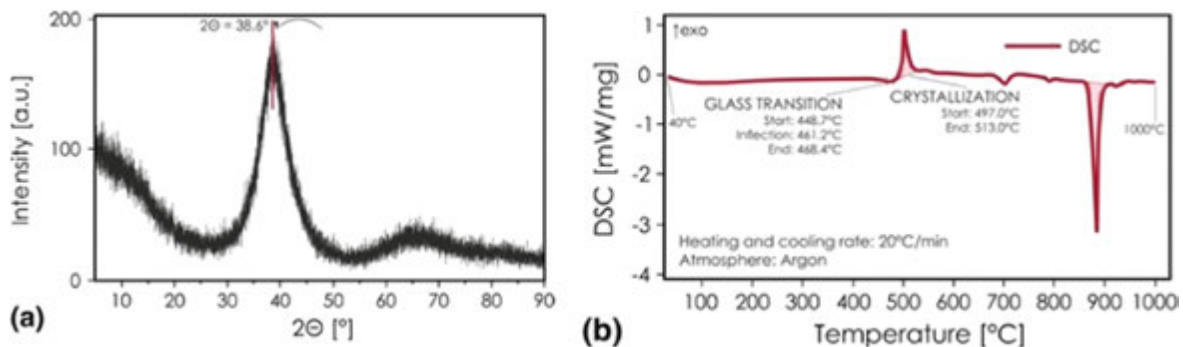


Fig. 4 XRD spectra (a) and DSC curve (b) of the $Zr_{43}Cu_{45}Al_{12}$ bulk metallic glass particles. Reproduced from Dąbrowa, J., Perriere, L., Stygar, M., *et al.*, 2015. Oxidation behavior of $Zr_{43}Cu_{45}Al_{12}$ bulk metallic glass at 400–525°C in air atmosphere. *Journal of Materials Engineering and Performance* 24 (12), 4863–4869.

aluminum matrix resulted in 25% improvement in compressive strength of composites when compared with the unreinforced Al. Wang *et al.* (2014) fabricated the $Al_{84}Gd_6Ni_7Co_3$ metallic glass-reinforced Al matrix composite using hot pressing followed by extrusion and reported their microstructures and tensile properties. As a comparison, addition of 20 vol% of $Al_{84}Gd_6Ni_7Co_3$ reinforcement into aluminum matrix resulted in an enhancement in the yield strength and tensile strength from 75 MPa, 120 MPa for pure Al to ~93 MPa, ~157 MPa respectively. Scudino *et al.* (2009) investigated the structural and mechanical properties of Al reinforced with mechanically alloyed $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ glassy particles using the powder metallurgy technique. A significant improvement in compressive strength was reported as compared to Al.

Reddy *et al.*, 2018c investigated the effect of milling time and concentration of amorphous alloy ($Cu_{50}Ti_{50}$) particles (0–15 wt%) on the microstructure and mechanical behavior of the aluminum metal matrix composites. The composites were synthesized by mechanical alloying and microwave sintering approach. The amorphous powders of $Cu_{50}Ti_{50}$ produced by ball milling were reinforced into the Al matrix. The test results have indicated that the incorporation of amorphous reinforcement into Al matrix results in improved hardness and compressive properties as compared to pure Al. Kim *et al.* (2012) used the powder metallurgy technique to fabricate brass-matrix composites by reinforcing brass matrix with $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ glassy particles (40 and 60 vol%). The results indicated that composites exhibited superior compressive strength as compared to brass material. Rezaei *et al.* (2016) studied microstructural and mechanical properties of aluminum-based composites reinforced with $Al_{65}Cu_{20}Ti_{15}$ metallic glass particles (0, 5, 10 and 15 vol%) through equal channel angular pressing (ECAP) method. Uniform distribution of metallic glass particles was observed with no interfacial reaction. The Al-10vol% $Al_{65}Cu_{20}Ti_{15}$ composite showed an increase of 52% in strength when compared to pure Al.

Production of Metallic Amorphous Particles/Bulk Metallic Glasses: Mechanical Alloying

Powder Metallurgy (PM) is recognized today as one of the most important manufacturing processes for producing industrial components. In particular, the growth of PM was phenomenal during the last quarter of the 20th century with the development of novel material processing techniques such as mechanical alloying (MA), atomization, rapid solidification process (RSP) etc., for powder production.

Among these, amorphous metals/metallic glasses are widely processed using mechanical alloying. Mechanical alloying is a powder metallurgy-based technique, which produces pure metallic powders through repeated cold welding, fracturing, and re-welding of the particles. Initially, raw metal powders of required composition were blended and mixed in a steel vial in a ball-mill. The mixed elemental powder particles are then subjected to extensive grinding in the vial using a grinding medium (usually stainless steel/tungsten carbide/alumina balls) and are agitated at high speeds for a desired period of time (high energy ball milling) until the required composition/structure/reaction is established. The amorphization during the mechanical alloying process occurs by solid-state interdiffusion reactions, which remove the long-range ordered crystal structure and gives rise to the amorphous structure. The basic concept of amorphization and its mechanism by high energy mechanical alloying is shown in Figs. 5 and 6 (Hellstern and Schultz, 1986; Suryanarayana, 2001).

Synthesis of Amorphous Particles Reinforced Al Composites

There are many techniques available to develop amorphous particles reinforced Al composites such as powder metallurgy, microwave sintering and infiltration casting (Lee *et al.*, 2004; Scudino *et al.*, 2009; Jayalakshmi *et al.*, 2013; Wang *et al.*, 2014; Issa *et al.*, 2017;

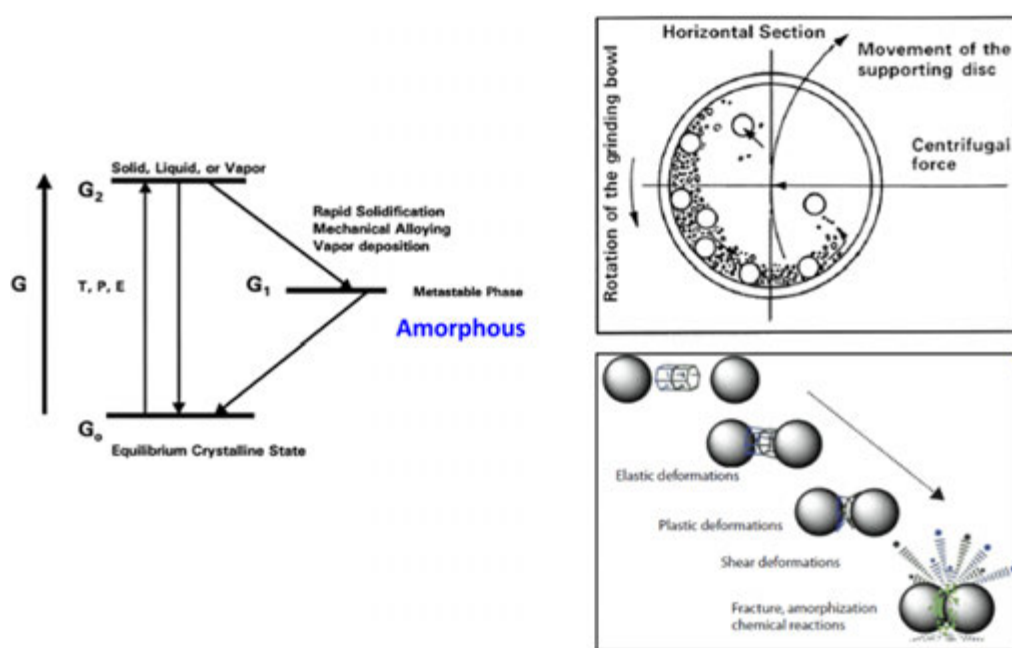


Fig. 5 Schematic showing the basic concept of amorphization (left), amorphization produced by the high energy ball-milling process (right). Reproduced from Suryanarayana, C., 2001. Mechanical alloying and milling. Progress in materials science 46 (1–2), pp. 1–184.

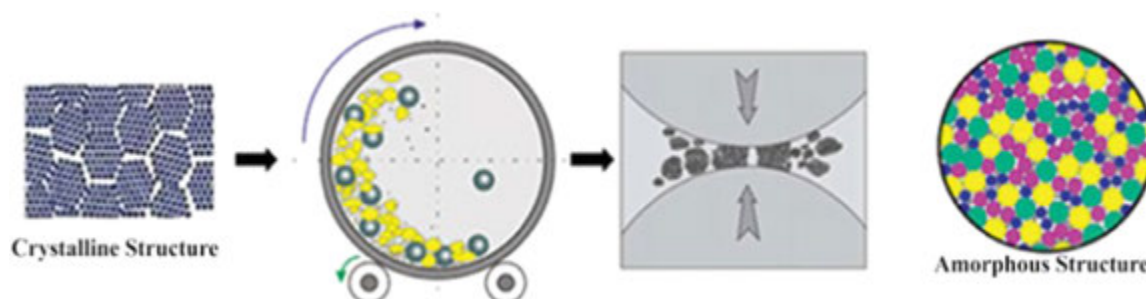


Fig. 6 Shows the schematic of the process from crystalline-to-amorphous transformation by high-energy ball-milling process. Reproduced from Suryanarayana, C., 2001. Mechanical alloying and milling. Progress in materials science 46 (1–2), pp. 1–184.

Reddy *et al.*, 2018c). Among those, the microwave sintering technique has emerged as a promising technique to develop high performance metal matrix composites (Jayalakshmi *et al.*, 2013). This technique carries salient advantages such as (1) rapid heating, (2) internal heating, (3) selected heating, (4) high heating efficiency, (5) rapid, (6) good temperature control, (7) high heating uniformity, and (8) clean energy source. A schematic diagram of the microwave sintering furnace is presented in Fig. 7.

The microwave sintering process sinters materials at higher temperatures within a relatively shorter period. Due to the shorter duration of processing time involved in this process, any undesirable reactions at the matrix/reinforcement interface are usually prevented. In contrast, in the conventional sintering methods, long duration of sintering time is necessary, which unavoidably gives rise to non-beneficial interfacial reactions.

During the synthesis process, the amorphous reinforcements are incorporated into Al- powder (matrix) at different volume fractions by the cold compaction method. Prior to cold compaction, the matrix and amorphous reinforcement are blended using the ball-milling technique to ensure uniform mixing. These powders are uniaxially compacted at a pressure of ~ 100 bar to obtain compact green billets of the desired size, which can be 36 mm in diameter and 40 mm in height. This green compact is then sintered for a pre-determined time using hybrid microwave sintering (MWS) methodology. The uniform heating of the billet using hybrid microwave helps in achieving near dense bulk nanocomposites as compared to the conventional sintering process. Moreover, the environmental friendly approach of hybrid microwave sintering helps in achieving better end-application properties with a massive reduction in processing time and costs. After this primary processing, the composites are subjected usually to the hot extrusion process at 350°C to obtain cylindrical rods of ~ 7 mm to 10 mm in diameter. The extruded rods were used for characterization and testing.

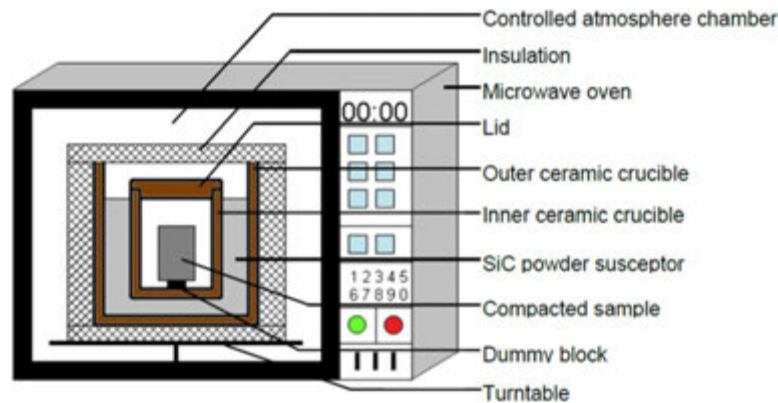


Fig. 7 Schematic diagram of microwave sintering process. Reproduced from Tun, K.S., 2009. Development and Characterization of New Magnesium Based Nanocomposites.

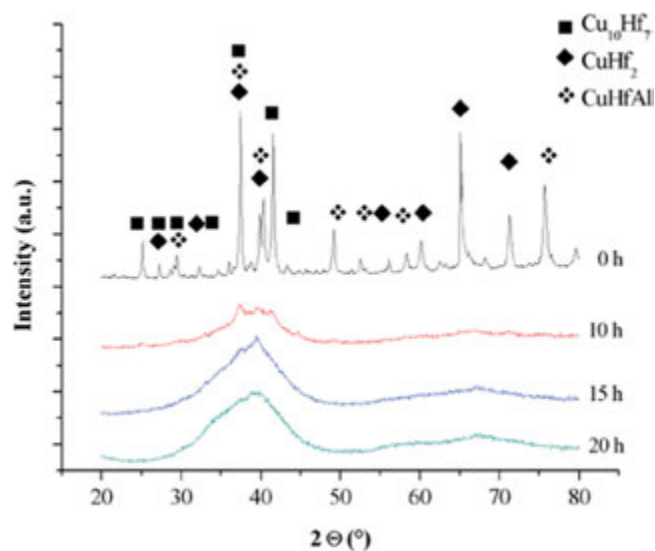


Fig. 8 XRD spectra of the $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ powders as a function of milling time. Reproduced from Svéda, M., Benke, M., András, R., 2013. Cu-Hf-Al amorphous/nanocrystalline composite particles produced by milling. *Építőanyag* 65 (2), 39–41.

Properties of Amorphous Particles Reinforced Aluminum Metal Composites

Amorphous particles reinforced aluminum (Al) metal matrix composites have been extensively developed by many researchers because of their superior properties compared to other aluminum alloys such as low density, attractive cost, high strength with lightweight and ease of fabrication. The copper (Cu), zirconium (Zr), niobium (Nb), nickel (Ni) etc., are the most common amorphous nanoparticles used as a reinforcement to synthesize amorphous particles reinforced Al composites.

Svéda *et al.* (2013) developed $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ amorphous composite particles using ball milling.

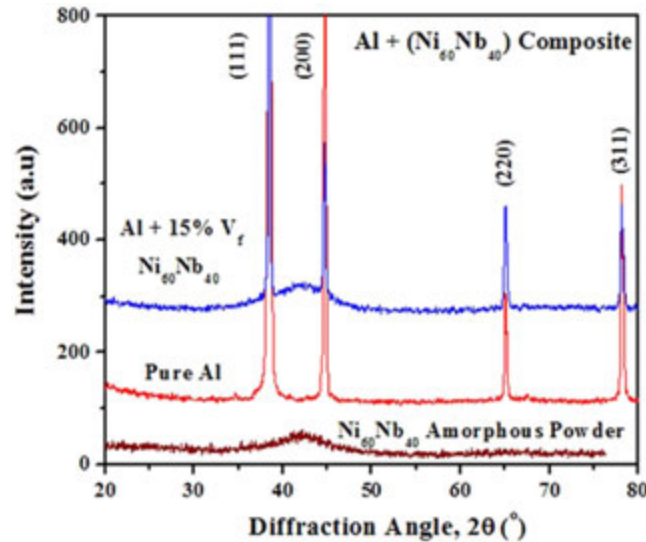


Fig. 9 X-ray patterns of pure Al and Al-15%VfNi₆₀Nb₄₀ amorphous alloy particle reinforced composite. Jayalakshmi, S., Singh, R.A., Gowrie, S., Lavanya, S., 2016. Microwave sintered aluminum composite with metallic glass reinforcement. In: Proceedings of the International Conference on Energy Efficient Technologies for Sustainability (ICEETS). IEEE.

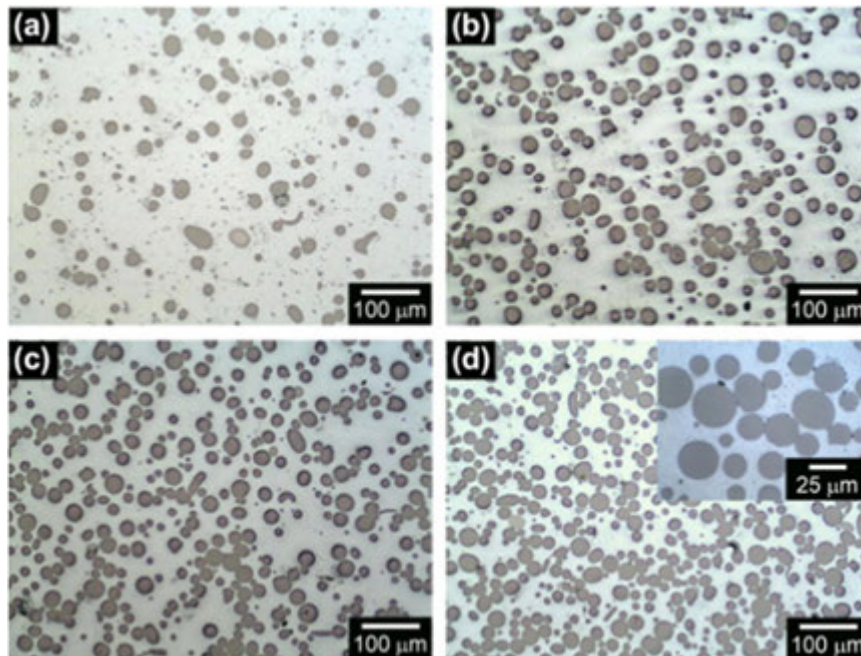


Fig. 10 Optical microscopy micrographs for the consolidated composites reinforced with (a) 10, (b) 20, (c) 30 and (d) 40 vol% of $\text{Fe}_{49.9}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.5}\text{Si}_{2.8}$ amorphous powder. Reproduced from Markó, D., Prashanth, K.G., Scudino, S., *et al.*, 2014. Al-based metal matrix composites reinforced with $\text{Fe}_{49.9}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.5}\text{Si}_{2.8}$ glassy powder: Mechanical behavior under tensile loading. Journal of Alloys and Compounds 615, S382–S385.

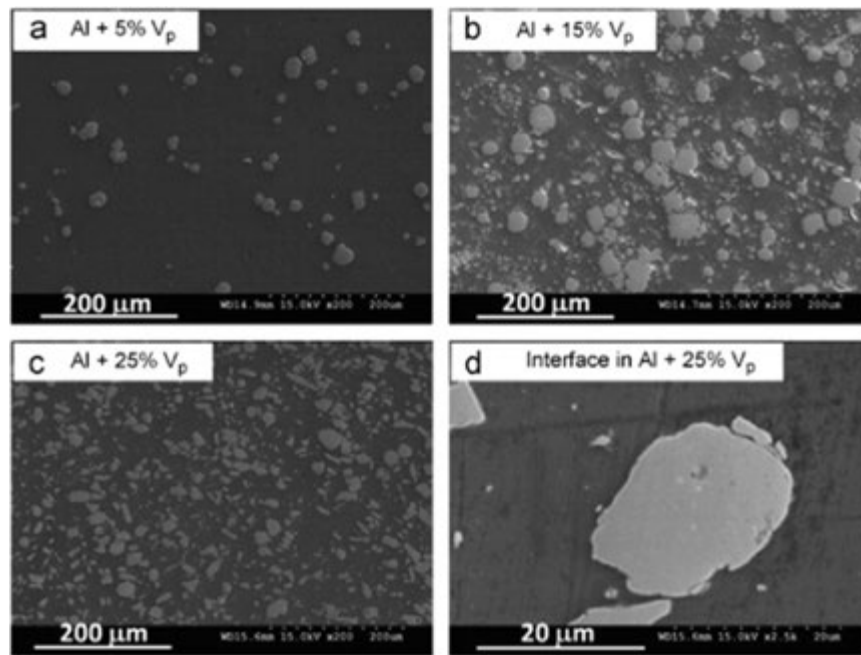


Fig. 11 FESEM images showing the uniform distribution of amorphous reinforcement particles in Al-composite with, (a) 5% V_p, (b) 15% V_p and (c) 25% V_p. Note the deformation of amorphous reinforcement particles at 25% V_p. (d) Representative image showing particle/matrix interface free of any interfacial products. Reproduced from Jayalakshmi, S., Singh, R.A., Gupta, M., 2018. Metallic glasses as potential reinforcements in al and mg matrices: A review. *Technologies* 6 (2), 40.

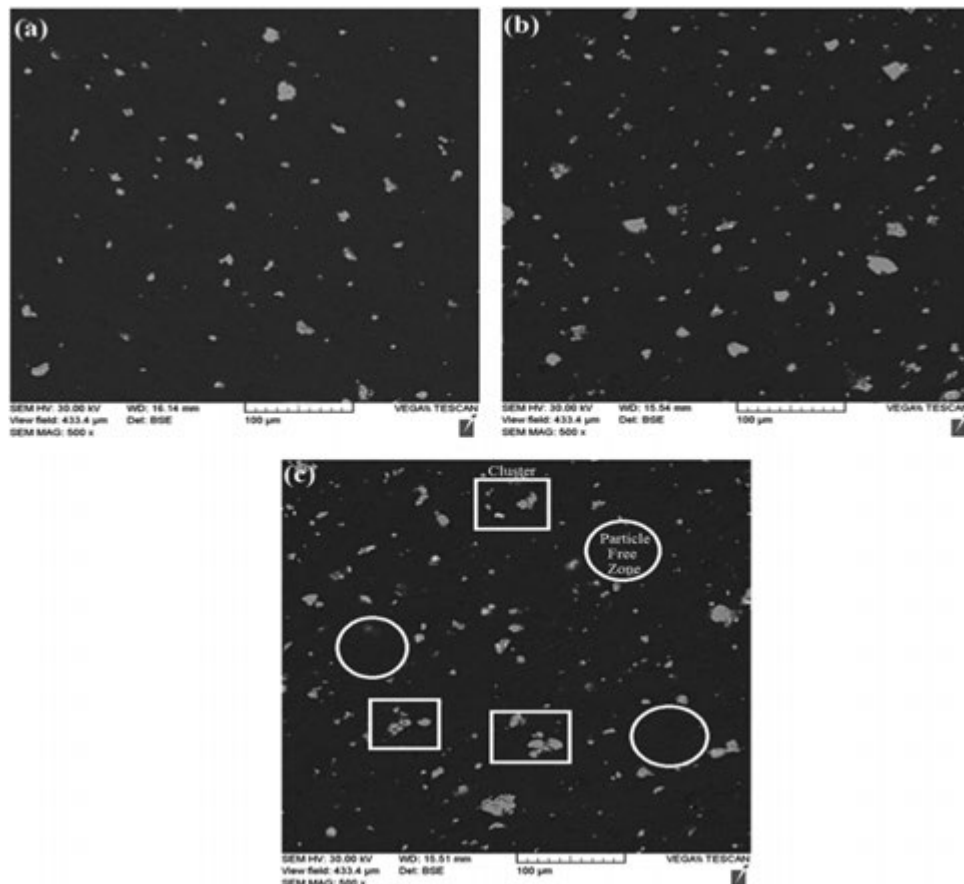


Fig. 12 SEM micrographs of the composites with (a) 5, (b) 10, and (c) 15 vol% of AMG reinforcement particles. Reproduced from Rezaei, M.R., Razavi, S.H., Shabestari, S.G., 2016. Development of a novel Al–Cu–Ti metallic glass reinforced Al matrix composite consolidated through equal channel angular pressing (ECAP). *Journal of Alloys and Compounds* 673, 17–27.

The effect of ball milling time on the structure of the amorphous composite was analysed. Fig. 7 depicts the XRD patterns of $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ composites. The XRD patterns of these amorphous reinforced Al composites reveal the broad peak formation in the range of 32° – 45° , which confirms the formation of the amorphous phase. Furthermore, the XRD spectra of $\text{Cu}_{54}\text{Hf}_{36}\text{Al}_{10}$ shown in Fig. 8 also explains the effect of milling time on the amorphous composite. The longer milling time for 20 h results in the formation of 95% of the amorphous fraction in the structure.

Jayalakshmi *et al.* (2016) incorporated $\text{Ni}_{60}\text{Nb}_{40}$ in pure aluminum using microwave sintering technique. The structural analysis indicates that are only crystalline peaks observed in the case of Al. On the other hand, the composite structure Al-15% $\text{Ni}_{60}\text{Nb}_{40}$ shows amorphous structure like $\text{Ni}_{60}\text{Nb}_{40}$ amorphous powder with no shift. (Fig. 9).

Markó *et al.* (2014) reported the effect of different volume fractions (10, 20, 30 and 40 vol%) of $\text{Fe}_{49.9}\text{Co}_{35.1}\text{Nb}_{7.7}\text{B}_{4.5}\text{Si}_{2.8}$ amorphous particles in Al matrix using planetary milling. Fig. 10 explains the optical microscopy of the extruded amorphous composites. The presence of dark particles in the matrix confirms the incorporation of amorphous reinforcements in the composites. Furthermore, uniform distribution of amorphous reinforcements without any agglomerations explain the effectiveness of mixing these powders using planetary milling.

Jayalakshmi *et al.* (2018) studied the Al-30 wt% $\text{Ni}_{60}\text{Nb}_{40}$ developed by mechanically alloying and sintering (823K) followed by hot pressing and extrusion. The study presents the scanning electron microscopy (SEM) of the 20 h milled $\text{Ni}_{60}\text{Nb}_{40}$ and the hot extruded nanocomposites (Fig. 11). The study illustrates the addition of amorphous reinforcements (bright particles) in the dark matrix Al without any side reaction zones. The $\text{Ni}_{60}\text{Nb}_{40}$ particles are randomly distributed, and the interface between the reinforcements and matrix is quite clear.

Rezaei *et al.* (2016) developed amorphous Al matrix composites using amorphous $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ reinforcement adopting equal channel angular pressing method. The SEM images of the developed amorphous composites presented in Fig. 12 shows a well-defined morphology without any fracture.

It can be observed that the amorphous reinforcement particles are homogeneously distributed in Al-5 vol% of $\text{Al}_{65}\text{Cu}_{20}\text{Ti}_{15}$ composite without any agglomeration (Fig. 12(a)). Furthermore, it is reported that the homogeneity of decreases with its increasing volume fraction of the reinforcement. The fact of decreasing the particle homogeneity can be regarded as the effect of clustering of reinforcement with the increasing volume fraction.

Zhang *et al.* (2018) reinforced Al with CuZrAl particles using mechanical alloying and spark plasma sintering. The microscopical analysis of the developed amorphous composite presented in Fig. 13 confirms that the Cu and Zr elements exhibit a uniform dispersion state. Therefore, it indicates that CuZrAl particles uniformly distributed in the Al matrix after the appropriate mixing time.

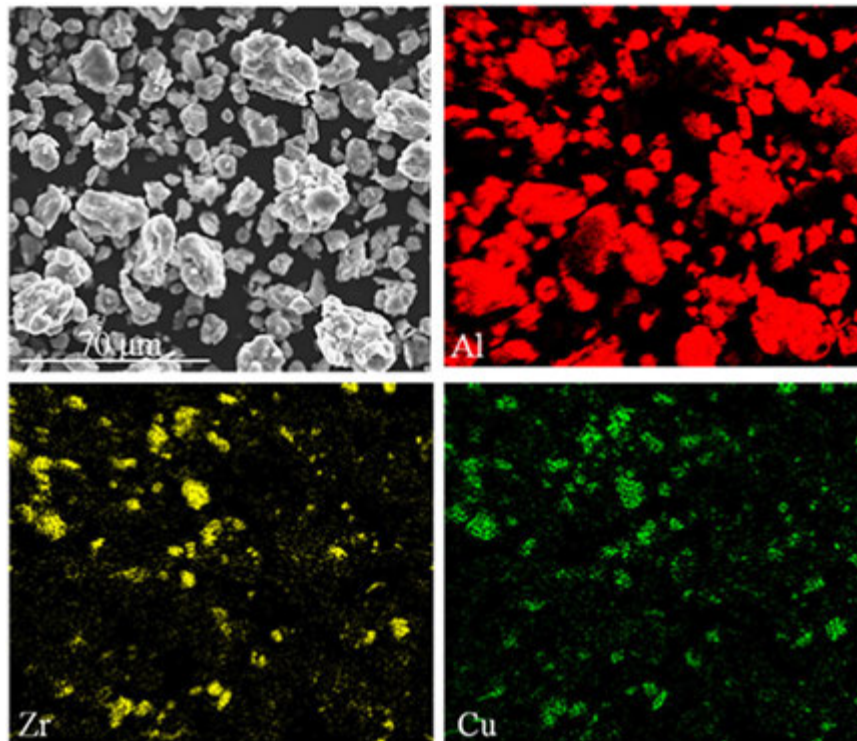


Fig. 13 Element mappings of 20 vol% CuZrAl/Al mixing powders and the corresponding micrograph. Reproduced from Zhang, L., Li, B., Wu, H., *et al.*, 2018. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Advanced Powder Technology* 29 (7), 1695–1702.

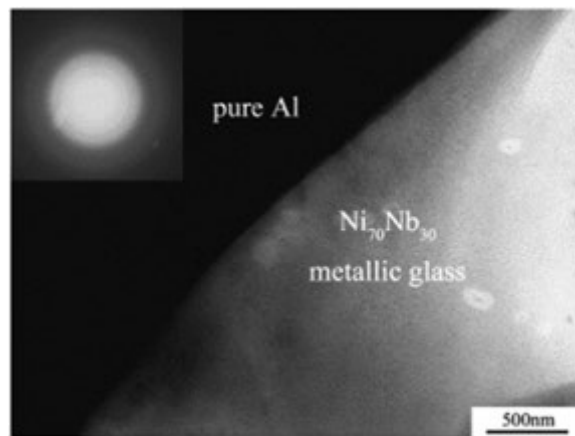


Fig. 14 TEM image showing the clear interface in the composite containing Al matrix reinforced with $\text{Ni}_{70}\text{Nb}_{30}$ metallic particles. Reproduced from Yu, P., Venkataraman, S., Das, J., *et al.*, 2007. Effect of high pressure during the fabrication on the thermal and mechanical properties of amorphous $\text{Ni}_{60}\text{Nb}_{40}$ particle-reinforced Al-based metal matrix composites. *Journal of materials research* 22 (5), 1168–1173.

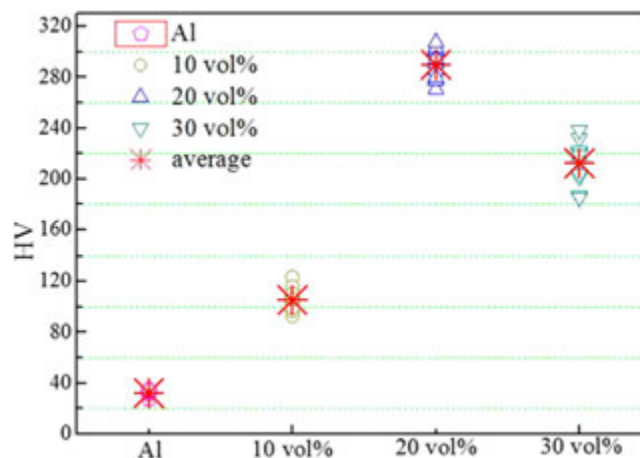


Fig. 15 Microhardness of the SPS-ed pure Al and Al-CuZrAl composites. Reproduced from Zhang, L., Li, B., Wu, H., *et al.*, 2018. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Advanced Powder Technology* 29 (7), 1695–1702.

Yu *et al.* (2007) synthesized Al- $\text{Ni}_{70}\text{Nb}_{30}$ amorphous composite using powder metallurgy route. The sintering temperature used in the study for the fabrication of the composites was below the melting temperature of Al (730K). The transmission electron microscopy (TEM) of the sintered sample shown in Fig. 13 explains the adequate bonding of $\text{Ni}_{70}\text{Nb}_{30}$ with the Al matrix and the formation of the pore-free surface and any reaction zones. Furthermore, selected area electron diffraction (SAED) pattern shown as an inset in Fig. 14 confirms the amorphous nature of the reinforcement.

Zhang *et al.* (2018) reinforced different vol% of the alloyed CuZrAl metallic amorphous particles into the Al matrix using spark plasma sintering technique. They evaluated the mechanical properties of the developed composites. It is reported that the microhardness of the composites increases with an increasing volume fraction of the amorphous (CuZrAl) reinforcement (Fig. 15). The maximum improvement in the microhardness was achieved at 20 vol%. Thereafter the value of microhardness showed a declining trend.

Jayalakshmi *et al.* (2013) studied the properties of Al-based composites developed by reinforcing Al matrix with amorphous $\text{Ni}_{60}\text{Nb}_{40}$ alloy powders using two directional microwave sintering technology followed by hot extrusion. It is reported that amorphous reinforcements contribute significantly to enhance the mechanical properties of the Al- $\text{Ni}_{60}\text{Nb}_{40}$ amorphous composites. The compressive yield strength of the developed composites demonstrated an increase of ~40 to 100% with the increasing vol% of the reinforcement ($\text{Ni}_{60}\text{Nb}_{40}$) when compared to pure Al (Fig. 16).

Rezaei *et al.* (2016) also reported in his findings of the compression behavior of the developed amorphous composites using various concentrations of amorphous reinforcement also called as amorphous bulk glasses (AMG). It is revealed that the strength of the developed composites exhibits a significant improvement with the increasing volume fraction of the amorphous reinforcement till 10 vol%. This improvement in strength is considered to be the effect of dispersion hardening effect of the hard

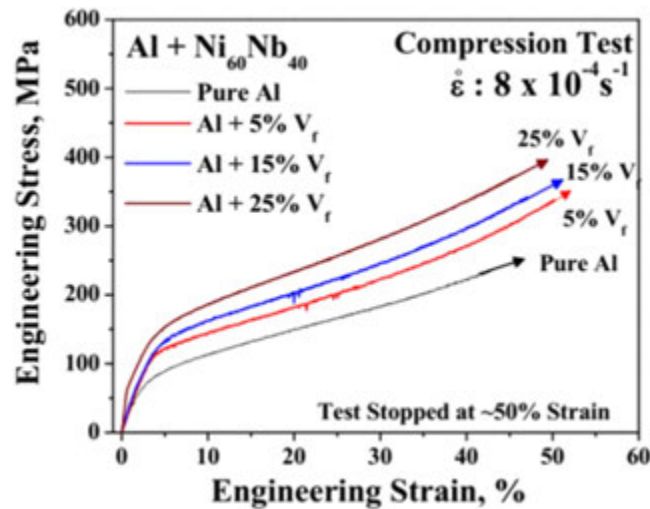


Fig. 16 Compression properties of pure aluminum reinforced with $\text{Ni}_{60}\text{Nb}_{40}$ (atomic pct.) amorphous alloy powder, synthesized by bi-directional microwave sintering. Reproduced from Jayalakshmi, S., Gupta, S., Seetharaman, S., Sahu, S., 2013. Structural and mechanical properties of $\text{Ni}_{60}\text{Nb}_{40}$ amorphous alloy particle reinforced Al-based composites produced by microwave-assisted rapid sintering. *Materials Science and Engineering: A* 581, 119–127.

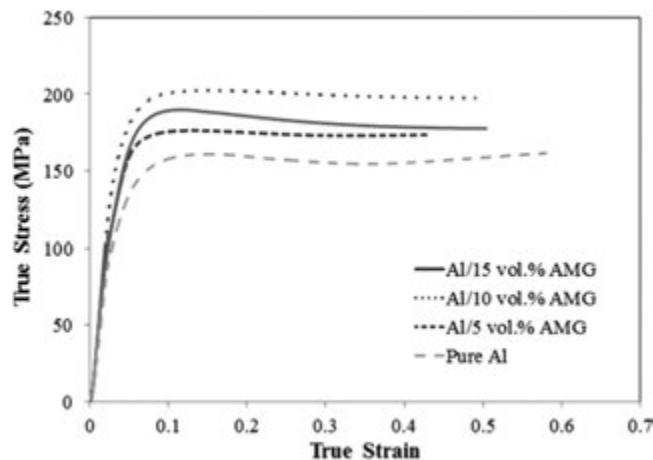


Fig. 17 True stress-true strain curves of consolidated pure Al and different Al/AMG composites. Reproduced from Rezaei, M.R., Razavi, S.H., Shabestari, S.G., 2016. Development of a novel Al–Cu–Ti metallic glass reinforced Al matrix composite consolidated through equal channel angular pressing (ECAP). *Journal of Alloys and Compounds* 673, 17–27.

reinforcement particles. Furthermore, it is also noticed that there is a decrease in the strength with further increase in the amount of reinforcement (Fig. 17).

The composite containing 15 vol% reinforcement (Al-15 vol%) shows a decrease in strength which can be associated to the agglomeration of the amorphous reinforcement. Clustering of the particles enhance the local stress concentration and hence provide the site for crack propagation in these amorphous reinforced composites. The crack propagation leads to work softening behavior.

Zhang *et al.* (2018) studied the tensile behavior of the developed $\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$ reinforced Al composites prepared by powder metallurgy route followed by hot pressing and extrusion. The tensile properties (Fig. 18) reveal a significant increase in the yield and ultimate strength of the developed composites compare with the pure Al. In addition, the ductility of the sample is reported to be reduced by 13%. The increase in the strength and decrease in the ductility is ascribed to the hard and brittle nature of the amorphous reinforcement.

Many studies have also conducted to understand the failure mechanism of amorphous particles reinforced Al-based composites. Fig. 19 shows the SEM images of the failed tensile samples having a different volume fraction of $\text{Ni}_{60}\text{Nb}_{40}$. A ductile fracture is reported in the tensile failure of the samples. It is observed that the amorphous reinforcement has a fine interfacial connection with the matrix without any noticeable debonding. The ductile fracture of the matrix without any cracks confirms the efficient load transfer of the amorphous reinforcement. Moreover, the cracking of amorphous particles (arrows in Fig. 19) is also noticed, which can be due to the localized stress distribution.

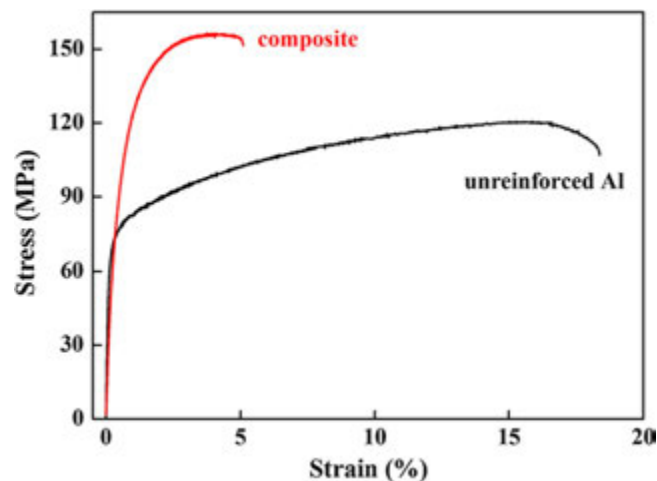


Fig. 18 Tensile stress-strain curves for the unreinforced Al matrix and for the composite reinforced with 20 vol% $\text{Al}_{84}\text{Gd}_6\text{Ni}_7\text{Co}_3$ particles. Reproduced from Zhang, L., Li, B., Wu, H., *et al.*, 2018. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Advanced Powder Technology* 29 (7), 1695–1702.

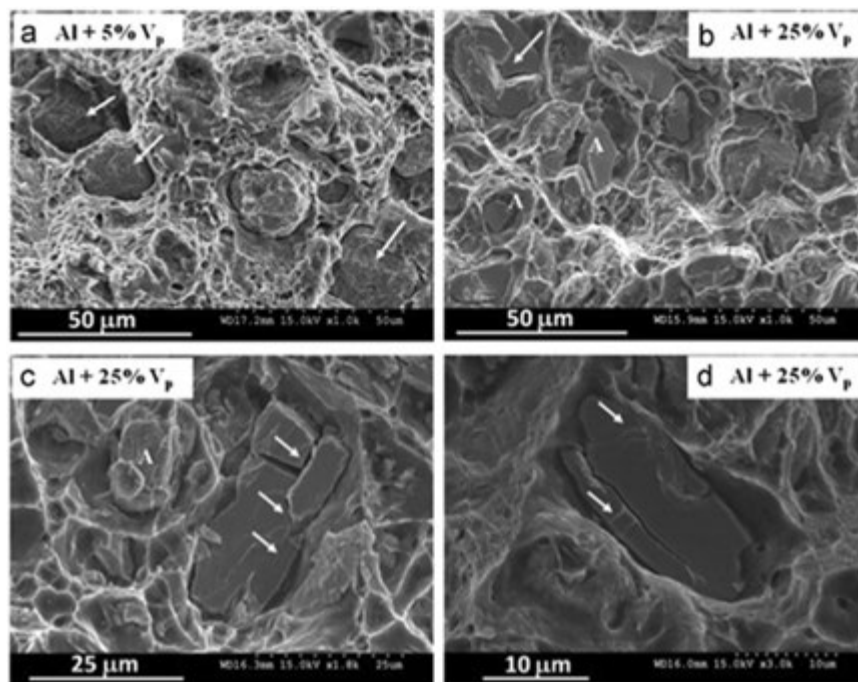


Fig. 19 Tensile fractographic images of Al-Ni₆₀Nb₄₀ amorphous particle reinforced composites. Reproduced from Jayalakshmi, S., Gupta, S., Seetharaman, S., Sahu, S., 2013. Structural and mechanical properties of Ni₆₀Nb₄₀ amorphous alloy particle reinforced Al-based composites produced by microwave-assisted rapid sintering. *Materials Science and Engineering: A* 581, 119–127.

In order to expand the area of utilization of amorphous particle reinforced composites, it is essential to evaluate their anticorrosion properties. Some reports are available in the literature addressing the corrosion resistance these composites. For example, the corrosion resistance of Al reinforced with CuZrAl is included here. The potentiodynamic polarization curves of the pure Al and the developed Al-CuZrAl amorphous composites are presented in Fig. 20. A comparison of anodic and cathodic curves shows that the corrosion resistance increases with the incorporation of CuZrAl reinforcement, suggesting an effective role of CuZrAl as an affective reinforcement to develop passive layer in the harsh corrosive environment. This is important when considering the application of these materials in an aggressive environment. Al-based composites are likely to be attacked by Cl⁻, which facilitates the formation of a passive layer of Al₂O₃ over the surface, which protect the composites from the adverse effect of corrosive species. Moreover, the presence of Zr in the composite leads to form Al₃Zr, which also enhances the anodic protection of the developed composites.

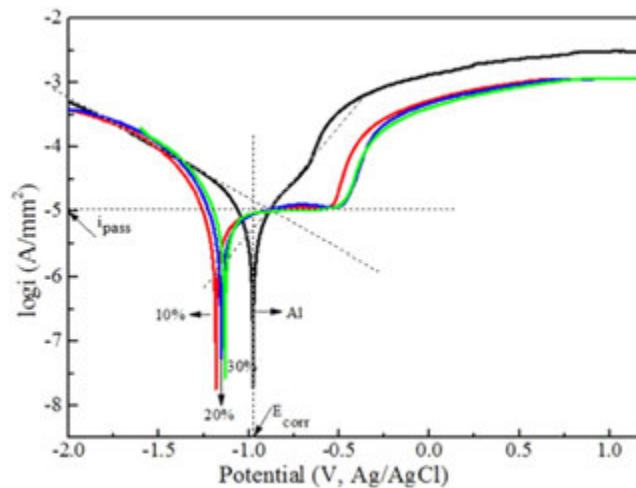


Fig. 20 Potentiodynamic polarization curves for the SPS-ed pure Al and Al-based composites reinforced with CuZrAl. Reproduced from Zhang, L., Li, B., Wu, H., *et al.*, 2018. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Advanced Powder Technology* 29 (7), 1695–1702.

Conclusions

The current article has explained in detail the introduction, synthesis techniques and properties of the amorphous reinforced Al base composites. Based on the reported research work, the following conclusions are made;

- Amorphous reinforced Al metal matrix composites possess a unique structure capable of demonstrating superior mechanical and anti-corrosive properties.
- Although amorphous reinforced Al metal matrix composites can be developed by many techniques, however, microwave sintering technique is more appealing due to its salient advantages over the conventional sintering approach.
- Amorphous reinforced Al metal matrix composites demonstrate decent mechanical properties well suited to many industrial applications.
- Finally, the promising anticorrosive properties of amorphous reinforced Al matrix composites extend their utilization to the marine application as well in addition to aerospace, automobile etc.

References

- Babalola, P.O., Bolu, C.A., Inegbenebor, A.O., Odunfa, K.M., 2014. Development of aluminium matrix composites: A review. *Online International Journal of Engineering and Technology Research* 2, 1–11.
- Dąbrowa, J., Perriere, L., Stygar, M., *et al.*, 2015. Oxidation behavior of $Zr_{43}Cu_{45}Al_{12}$ bulk metallic glass at 400–525°C in air atmosphere. *Journal of Materials Engineering and Performance* 24 (12), 4863–4869.
- El-Labban, H.F., Abdelaziz, M., Mahmoud Essam, R.I., 2014. Coating of 6028 aluminum alloy using aluminum piston alloy and Al-Si alloy-based nanocomposites produced by the addition of Al-Ti5-B1 to the matrix melt. *Metallurgical and Materials Transactions B* 45 (5), 1608–1614.
- Hatch, J.E., 1984. *Aluminum: Properties and Physical Metallurgy*. ASM International.
- Hellstern, E., Schultz, L., 1986. Amorphization of transition metal Zr alloys by mechanical alloying. *Applied Physics Letters* 48 (2), 124–126.
- Issa, H.K., Taherizadeh, A., Maleki, A., Ghaei, A., 2017. Development of an aluminum/amorphous nano-SiO₂ composite using powder metallurgy and hot extrusion processes. *Ceramics International* 43 (17), 14582–14592.
- Jayalakshmi, S., Gupta, S., Seetharaman, S., Sahu, S., 2013. Structural and mechanical properties of $Ni_{60}Nb_{40}$ amorphous alloy particle reinforced Al-based composites produced by microwave-assisted rapid sintering. *Materials Science and Engineering: A* 581, 119–127.
- Jayalakshmi, S., Singh, R.A., Gowrie, S., Lavanya, S., 2016. Microwave sintered aluminium composite with metallic glass reinforcement. In *Proceedings of the International Conference on Energy Efficient Technologies for Sustainability (ICEETS)*. IEEE.
- Jayalakshmi, S., Singh, R.A., Gupta, M., 2018. Metallic glasses as potential reinforcements in Al and Mg matrices: A Review. *Technologies* 6 (2), 40.
- Jayalakshmi, S., Gupta, M., 2015. Light metal matrix composites with amorphous alloys/bulk metallic glass reinforcements (BMG). In *Metallic Amorphous Alloy Reinforcements in Light Metal Matrices*. Springer. pp. 85–106.
- Jiang, X., Galano, M., Audebert, F., 2014. Extrusion textures in Al, 6061 alloy and 6061/SiCp nanocomposites. *Materials Characterization* 88, 111–118.
- Kim, J.Y., Scudino, S., Kühn, U., *et al.*, 2012. Production and characterization of brass-matrix composites reinforced with $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ glassy particles. *Metals* 2 (2), 79–94.
- Svéda, M., Benke, M., András, R., 2013. Cu-Hf-Al amorphous/nanocrystalline composite particles produced by milling. *Építőanyag* 65 (2), 39–41.
- Lee, M.H., Kim, J.-H., Park, J.C., *et al.*, 2004. Fabrication of Ni–Nb–Ta metallic glass reinforced Al-based alloy matrix composites by infiltration casting process. *Scripta Materialia* 50 (11), 1367–1371.
- Lloyd, D., 1994. Particle reinforced aluminium and magnesium matrix composites. *International Materials Reviews* 39 (1), 1–23.
- Luborsky, F., 1983. *Amorphous Metallic Alloys*. 1983. Butterworth and Co. Ltd. p. 534.
- Markó, D., Prashanth, K.G., Scudino, S., *et al.*, 2014. Al-based metal matrix composites reinforced with $Fe_{49.5}Co_{35.1}Nb_{7.7}B_{4.5}Si_{2.8}$ glassy powder: Mechanical behavior under tensile loading. *Journal of Alloys and Compounds* 615, S382–S385.

- Miracle, D., 2005. Metal matrix composites – From science to technological significance. *Composites science and technology* 65 (15–16), 2526–2540.
- Polmear, I., 1995. Metallurgy of the lightmetals. In: *Light Alloys*, third ed. London: Edward Arnold.
- Pradhan, S., Jena, S.K., Patnaik, S.C., Swain, P.K., Majhi, J., 2015. Wear characteristics of Al-AlN composites produced in-situ by nitrogenation. In *Proceedings of the IOP Conference Series: Materials Science and Engineering*. IOP Publishing.
- Rawal, S.P., 2001. Metal-matrix composites for space applications. *JOM* 53 (4), 14–17.
- Reddy, M.P., Shakoor, R.A., Parande, G., *et al.*, 2017a. Enhanced performance of nano-sized SiC reinforced Al metal matrix nanocomposites synthesized through microwave sintering and hot extrusion techniques. *Progress in Natural Science: Materials International* 27 (5), 606–614.
- Reddy, M.P., Ubaid, F., Shakoor, R.A., *et al.*, 2017b. Effect of reinforcement concentration on the properties of hot extruded Al-Al₂O₃ composites synthesized through microwave sintering process. *Materials Science and Engineering: A* 696, 60–69.
- Reddy, M.P., Himyan, M.A., Ubaid, F., *et al.*, 2018a. Enhancing thermal and mechanical response of aluminum using nanolength scale TiC ceramic reinforcement. *Ceramics International* 44 (8), 9247–9254.
- Reddy, M.P., Manakari, V., Parande, G., *et al.*, 2018b. Enhancing compressive, tensile, thermal and damping response of pure Al using BN nanoparticles. *Journal of Alloys and Compounds* 762, 398–408.
- Reddy, M.P., Ubaid, F., Shakoor, R.A., Mohamed, A.M.A., 2018c. Microstructure and mechanical behavior of microwave sintered Cu₅₀Ti₅₀ amorphous alloy reinforced Al metal matrix composites. *JOM* 70 (6), 817–822.
- Rezaei, M.R., Razavi, S.H., Shabestari, S.G., 2016. Development of a novel Al–Cu–Ti metallic glass reinforced Al matrix composite consolidated through equal channel angular pressing (ECAP). *Journal of Alloys and Compounds* 673, 17–27.
- Scudino, S., Liu, G., Prashanth, K.G., *et al.*, 2009. Mechanical properties of Al-based metal matrix composites reinforced with Zr-based glassy particles produced by powder metallurgy. *Acta Materialia* 57 (6), 2029–2039.
- Sheng, H.W., Luo, W.K., Alamgir, F.M., Bai, J.M., Ma, E., 2006. Atomic packing and short-to-medium-range order in metallic glasses. *Nature* 439 (7075), 419.
- Stojanović, B., Ivanović, L., 2015. Application of aluminium hybrid composites in automotive industry. *Tehnički Vjesnik* 22 (1), 247–251.
- Surappa, M., 2003. Aluminium matrix composites: Challenges and opportunities. *Sadhana* 28 (1–2), 319–334.
- Suryanarayana, C., 2001. Mechanical alloying and milling. *Progress in Materials Science* 46 (1–2), 1–184.
- Telford, M., 2004. The case for bulk metallic glass. *Materials Today* 7 (3), 36–43.
- Wahyuni, N., Nur, R., Renreng, I., Adnan, M., 2019. Effect of adding SiC on resistance wear and hardness through stir casting of aluminum matrix composites. In *Proceedings of AIP Conference*. AIP Publishing.
- Wang, Z., Prashanth, K.G., Scudino, S., *et al.*, 2014. Tensile properties of Al matrix composites reinforced with in situ devitrified Al₈₄Gd₆Ni₇Co₃ glassy particles. *Journal of Alloys and Compounds* 586, S419–S422.
- Yu, P., Venkataraman, S., Das, J., *et al.*, 2007. Effect of high pressure during the fabrication on the thermal and mechanical properties of amorphous Ni₆₀Nb₄₀ particle-reinforced Al-based metal matrix composites. *Journal of Materials Research* 22 (5), 1168–1173.
- Zhang, L., Li, B., Wu, H., *et al.*, 2018. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Advanced Powder Technology* 29 (7), 1695–1702.

Metal Matrix Syntactic Composites

Vyasraj Manakari, Gururaj Parande, and Manoj Gupta, Department of Mechanical Engineering, National University of Singapore, Singapore

Mrityunjay Doddamani, Advanced Manufacturing Laboratory, National Institute of Technology Karnataka, Surathkal, Karnataka, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

The continuous depletion of fossil fuels and serious environmental problems caused by the ever-increasing global economy have triggered severe threats to the survival and development of humankind. Consequently, exploring novel materials with multifunctionality is fundamental for the sustainable development of the economy and society (Wu *et al.*, 2019). The traditional approach to the development of materials and structures addresses the load carrying function and other functional requirements separately, resulting in a suboptimal load-bearing structure with add-on attachments that perform the non-structural functions with the penalty of added weight. Recently, however, there has been an increased interest in the development of multifunctional materials that are designed to perform (1) multiple structural functions simultaneously, (2) combined non-structural and structural functions, or (3) both.

In this regard, lightweight high-performance composites gain attention due to their higher specific properties, ease of fabrication, and tailorability in properties (Gupta and Wong, 2015; Thornby *et al.*, 2019, 2021; Parande *et al.*, 2020). One of the easiest ways of decreasing the weight of the structures is to remove material from them. This can be done by imparting air packets inside the materials in the form of porosity. In this context, these materials can be classified as open cell and closed cell foam composites (Patil *et al.*, 2019a,b; Singh *et al.*, 2019; Doddamani, 2020). The open cell foams consist of channels or pockets of air throughout the material's microstructure (Montminy *et al.*, 2004; Jang *et al.*, 2008). Although open cell foam method reduces weight, it can potentially undermine the structure's structural integrity as there is a lack of controllability of the pores (Bharath *et al.*, 2020, 2021a,b; Bonthu *et al.*, 2020; Gupta and Doddamani, 2020; Sailesh *et al.*, 2021).

One of the novel ways of imparting porosity in structures is to enclose the porosity inside stiff shells. These materials are called syntactic foams, wherein hollow microballoons are enclosed inside a matrix material (Doddamani *et al.*, 2011; Manakari *et al.*, 2015; Waddar *et al.*, 2018, 2019). Incorporating porosity through hollow particles instead of embedding air/gas voids provides a reinforcing effect to each pore and imparts properties similar or superior to what would be found in monolithic cellular materials, in particular metallic foams (Omar *et al.*, 2015). The incorporation of porosity in material makes the material lightweight and enhances compressibility. Energy absorption and ductility can be further enhanced by increasing the extent of porosity (Ashrith *et al.*, 2019; Manakari *et al.*, 2019; Shahapurkar *et al.*, 2019). Open cell foams lack strength and modulus limiting their application. Metal matrix syntactic foams (MMSFs) exhibit superior mechanical properties due to closed cell structure for the same amount of porosity (Rohatgi *et al.*, 2011). The plateau strength and densification strain are also closely related to porosity in the foam composite. Lightweight foam composites with high energy absorption capacity can be used to reduce shock loadings against impact, for example, in mining and automotive industries (Tao *et al.*, 2009).

An illustration of a syntactic foam microstructure is presented in Fig. 1. Several phases exist in the microstructure, as shown in the Fig. 1. The varying parameters in synthesizing syntactic foams include choosing the matrix and microballoon materials, the volume fraction, and the density of the microballoons. The density of the microballoons is determined by the wall thickness parameter of the reinforcing microballoon. The microballoon wall thickness is characterized by radius ratio (η) as

$$\eta = R_i/R_o$$

where R_i and R_o are the inner and outer radii of the microballoon. Fig. 2 shows the illustration of the variation in the wall thickness parameter of the microballoon. So, by controlling the volume fraction and wall thickness parameter of the microballoon, the effective mechanical, thermal, biological properties of the composites can be tailored. This tailorability capability of the syntactic foams makes it an ideal candidate to be used in weight saving applications (Fig. 3).

Hollow Particles

Fly Ash Cenospheres

The presence of hollow particles has traditionally exhibited isotropic properties, better compressive strength and modulus, high strength to weight ratio, and good energy absorption (Rohatgi *et al.*, 2011). However, cost remains a significant barrier in the widespread use of metal matrix composite components in the industry. The utilization of fly ash particles, a by-product of the coal-fired power plants, as reinforcement can drastically reduce the cost of the metal matrix composites. Moreover, the application of fly ash cenosphere particles in the syntactic foam system effectively utilizes industrial waste, thereby reducing carbon dioxide emissions. Fly ash cenospheres are generally gray to buff in color, between 0.5 and 100 μm in diameter, with silica and alumina being the major constituents. The fly ash particles are like hollow micro balloons with a true density of 0.4–1 g/cc and are spherical where the sphericity is very close to 100%. An example of cenospheres is presented in Fig. 4(a). The low density encourages its usage in developing lightweight composites (Rohatgi *et al.*, 2006). Composite foams have been prepared in the past with fly ash

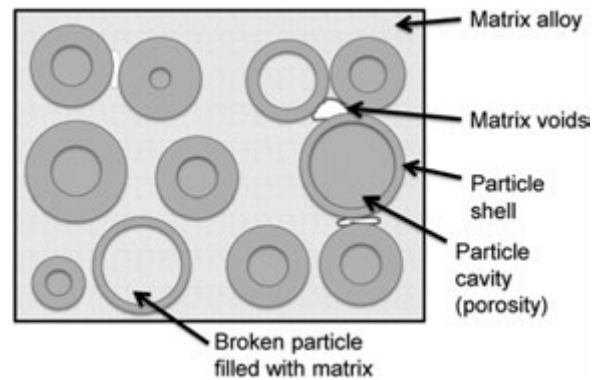


Fig. 1 Schematic illustration of syntactic foam microstructure showing various phases and two types of voids. Reproduced from Gupta, N., *et al.*, 2012. Magnesium matrix composite foams—density, mechanical properties, and applications. *Metals* 2 (3), 238–252.

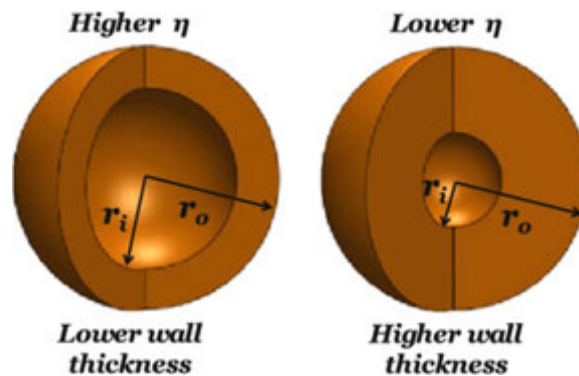


Fig. 2 Illustration of change in wall thickness and radius ratio, η , in hollow particles. Reproduced from Shunmugasamy, V.C., *et al.*, 2012. Thermal expansion behavior of hollow glass particle/vinyl ester composites. *Journal of Materials Science* 47 (14), 5596–5604.

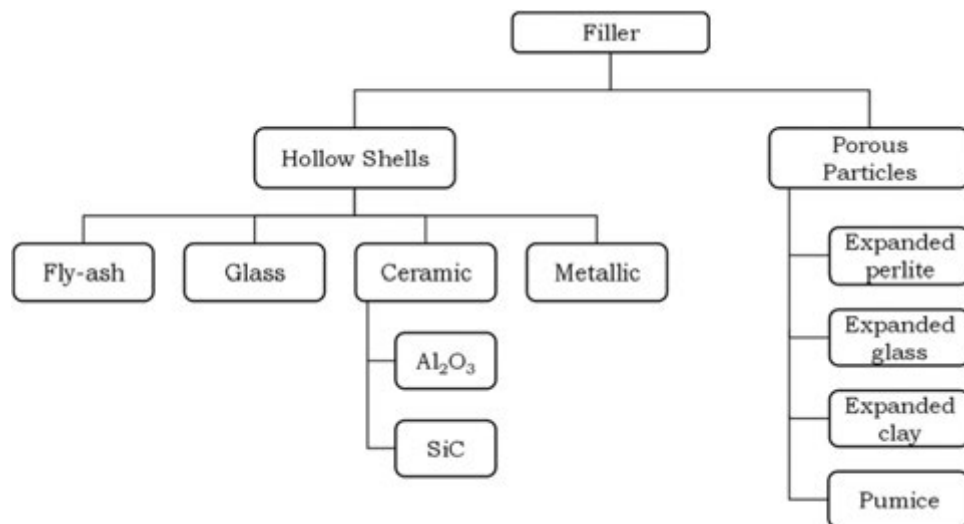


Fig. 3 Typical hollow particles used in MMSFs.

particles into the metallic and polymeric matrices (Gupta *et al.*, 2013; Gupta and Rohatgi, 2014). Some of the cenospheres may have porosity embedded in their shell, as seen in Fig. 4(b) (Gupta *et al.*, 2012).

Many researchers have studied the effect of fly ash particles in aluminum and magnesium matrix composites. Owing to their energy-intensive production methods, the replacement of part of Al and Mg by fly ash particles promises considerable energy savings (Rohatgi *et al.*, 1996). Metal matrix syntactic foams (MMSFs) with hollow particle volume fractions as high as 60% have been synthesized (Gupta *et al.*, 2012). At such a high-volume fraction, the syntactic foams exhibit a density in the range 1–1.5 g/cc, which is directly comparable with the polymer matrix composites. The higher melting points, ductility, and modulus of the MMSFs make them more desirable when compared to

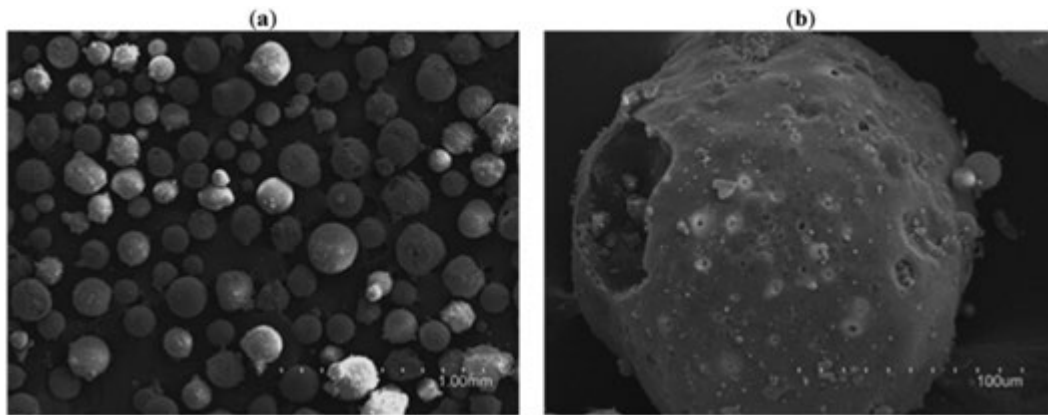


Fig. 4 (a) Fly ash cenospheres; (b) Defects present in some cenospheres may include irregular shape, nonuniform wall thickness, and porous walls. Reproduced from Gupta, N., *et al.*, 2012. Magnesium matrix composite foams—density, mechanical properties, and applications. *Metals* 2 (3), 238–252.

polymer matrix composites (Gupta *et al.*, 2012). Over the years, the concept of syntactic foams is very well established for aluminum and polymer systems (Mukai *et al.*, 1999; Kanahashi *et al.*, 2001; Wen *et al.*, 2004; Solórzano *et al.*, 2008). The aluminum matrix fly ash composites have been used to fabricate various components like pistons, connecting rods, and engine covers (Rohatgi *et al.*, 1996; Matli *et al.*, 2020a). The research on magnesium matrix syntactic foams is increasing as the density of magnesium is $\sim 35\%$ lower than aluminum (Hartmann *et al.*, 1998; Manakari *et al.*, 2016, 2017, 2020; Matli *et al.*, 2020b; Prasad *et al.*, 2020; Padnuru Sripathy *et al.*, 2021).

Although cenospheres possess numerous advantages, the lack of ability to control their production tends to result in inherent randomness in cenosphere quality. Examples of potential defects include variability in wall thickness as well as the presence of particle porosity. The former can result in “premature” failure of the hollow particle, either in processing or in the initial stages of loading. The presence of surface porosity can result in the filling of hollow particles during processing, thereby eliminating the contribution of the hollow particle to a lower overall foam density as well as an increase in energy absorbing capability.

Engineered Hollow Particles

Besides the massive popularity of lightweight composites, the interest in hollow particles is also ever increasing for several applications, and several techniques are now available to synthesize such particles of controlled composition and quality (Károly and Szépvölgyi, 2003; Hyodo *et al.*, 2005; Watanabe *et al.*, 2007). The engineered hollow particles produced from these methods are typically called microballoons. Microballoon is often used to reference hollow particles that are not created as a by-product of the combustion process, i.e., cenospheres. A variety of techniques are used to produce microballoons with controlled sizes and properties. For example, in the late 1980s, a method for producing microballoons was developed that started introducing polystyrene balls into an air current above a fluidized bed. The balls were then coated with a suspension of metal or ceramic powder and binder. After the desired coating thickness was reached, the balls were subjected to heat treatment which burned off the polystyrene and other organic components. The resulting particles were then sintered just below the melting temperature to form a hard and cohesive shell. This approach is currently used by Hollomet GmbH (Dresden, Germany) to make both particles and foams in a variety of materials. Further details of this method may be found in Öechsner and Augustin (2009).

Similarly, Deep Spring Technology (Toledo, OH) has developed the capability of producing a broad variety of ceramic and metal hollow particles suitable for metal matrix syntactic composites. They have matured the manufacturing process such that hermetic (gas tight) ceramic hollow particles made of silicon carbide, boron carbide, and alumina oxide are produced, which now are commercially available. The increased size range and uniformity of the current hollow particles may be useful in developing lightweight composites with a higher level of strength and modulus than glass or fly ash hollow particles. Hollow spheres of diameters ranging from less than 1 mm to more than 10 mm are commercially available, as shown in Fig. 5. Fig. 5 also shows a uniform wall thickness in hollow particles, with a wall thickness to outer diameter ratio of about 32:1.

In addition to methods described above, several novel techniques have been developed to produce a variety of ceramic, carbon and glass hollow particles such as powder slurry method, ion extraction of colloidal alumina sols, ceramic slurry technique, microfluidic process and solid templating technique which aim at improving the cost, quality and reproducibility of the hollow fillers. Usually, engineered hollow particles have controlled structure and properties and offer better properties compared to fly ash cenospheres. In addition, their surfaces can be engineered to increase compatibility with the matrix metal or alloy.

Processing Techniques

The mechanical properties of the MMSFs mainly depend on the uniform dispersion of reinforcements within the metal matrix. The higher the hollow particle distribution, the more is the synthesis technique considered efficient. The methods to obtain syntactic foams are stir casting, pressure infiltration, powder metallurgy, and disintegrated melt deposition (Fig. 6).

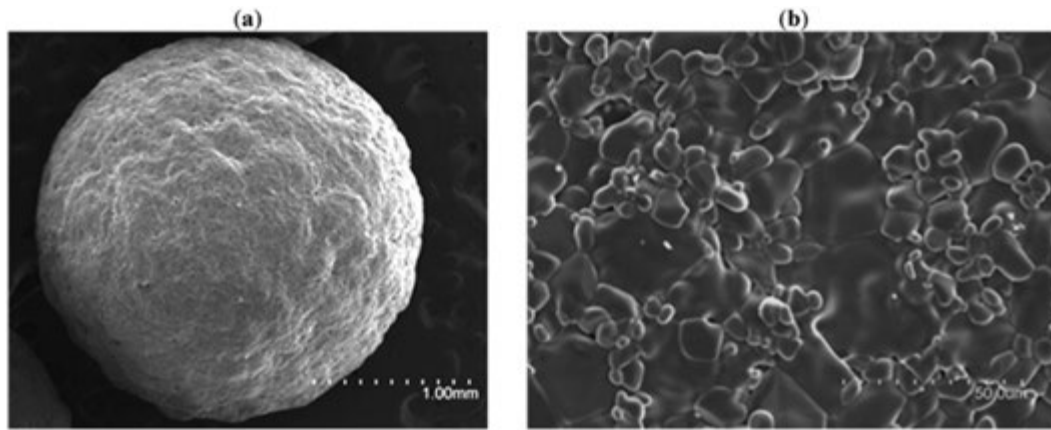


Fig. 5 (a) Alumina hollow particle; and (b) the surface of the alumina particle (Courtesy Deep Springs Technologies, Toledo, OH, USA).

Stir Casting

In the stir casting technique, the stirring of molten metal is realized by using a high shear impeller with particles into the vortex formed in the melt. The molten metal is immediately poured into a sand mold and further allowed to cool and solidify. Stir casting is a low cost process and requires basic foundry infrastructure (Daoud *et al.*, 2007). However, the flotation of low-density hollow particles is a major drawback in this process primarily when the particle volume fraction is low. Wetting of particles with liquid melts and chances of particle fracture for high volume fraction are also significant disadvantages of this process (Rohatgi *et al.*, 2011). Some researchers have also suggested using coatings to seal the porosity of the hollow fly ash micro balloons (Rajan *et al.*, 2007; Surappa, 2008).

Pressure Infiltration

In the pressure infiltration technique, a preform of loosely packed particles is placed in mould (Liu *et al.*, 2012). The molten metal matrix is infiltrated into the mold with the application of either high pressure or vacuum or both to form a near-net-shaped syntactic foam component by filling the inter-particulate spacing (Zhang and Zhao, 2007). Infiltration of loose beds of cenospheres with molten alloys to form syntactic foams can eliminate the need for preform preparation. To avoid incomplete infiltration and the freeze choking of the melt, establishing control over particle preheat temperature and melt superheat temperature is critical (Rohatgi *et al.*, 2011). The major advantages of this process are (1) synthesis of syntactic foams with higher particle volume fraction of up to 70% with low porosity and (2) near-net-shaped components. The limitations of this technique are that high infiltration pressure can cause fracture of hollow particles and infiltration of liquid metal into the hollow spaces of the cenospheres. On the other hand, low infiltration pressure may result in high residual porosity due to incomplete filling of pores (Rohatgi *et al.*, 2011).

Powder Metallurgy

Powder metallurgy is a type of solid-phase processing method. This technique is very flexible as it can synthesize composites with a wide spectrum of particle volume fractions. The hollow particles are thoroughly mixed with the metal matrix material and further compacted under pressure. The resulting component is known as a “green compact”. This green compact is sintered using either conventional or microwave assisted sintering techniques to obtain a syntactic foam (Hrairi *et al.*, 2009; Gupta and Wong, 2015). The powder metallurgy technique can synthesize reactive materials, which are not controllable in liquid-phase processing. During the synthesis of high particle volume fraction composites, the fracture of weak hollow particles was observed during the compaction stage. Hence, this method is best suited to synthesize low fly ash volume fraction syntactic foams (Rohatgi *et al.*, 2011).

Disintegrated Melt Deposition (DMD)

DMD is a unique cost-effective technique that brings together the advantages of conventional casting and spray processing, utilizing lower impinging gas jet velocities and higher superheat temperatures to produce bulk composite material (Fig. 7). Synthesis of hollow particle reinforced magnesium composites using DMD technique involves heating the reinforcement powder and magnesium chips/turnings in a multi-layered ordering to a superheat temperature (750°C) in a graphite crucible with a resistance heating furnace under the influence of an inert argon gas atmosphere. The crucible is equipped with an arrangement for bottom pouring. Upon reaching the superheat temperature, the molten slurry is stirred using a Zirtex coated steel impeller for 5 min at approximately 450 rpm for uniform distribution of hollow particles in the metallic matrix. The stirring also ensures homogeneity in crucible temperature. The composite melt is disintegrated by two jets of argon gas orientated normal to the melt stream before being deposited onto a metallic substrate to obtain a preform. Fine equiaxed grains, uniform distribution of reinforcements, and faster solidification of atomized melt leading to decreased porosity and improved properties are some advantages of the DMD technique. The material wastage is also very minimal in

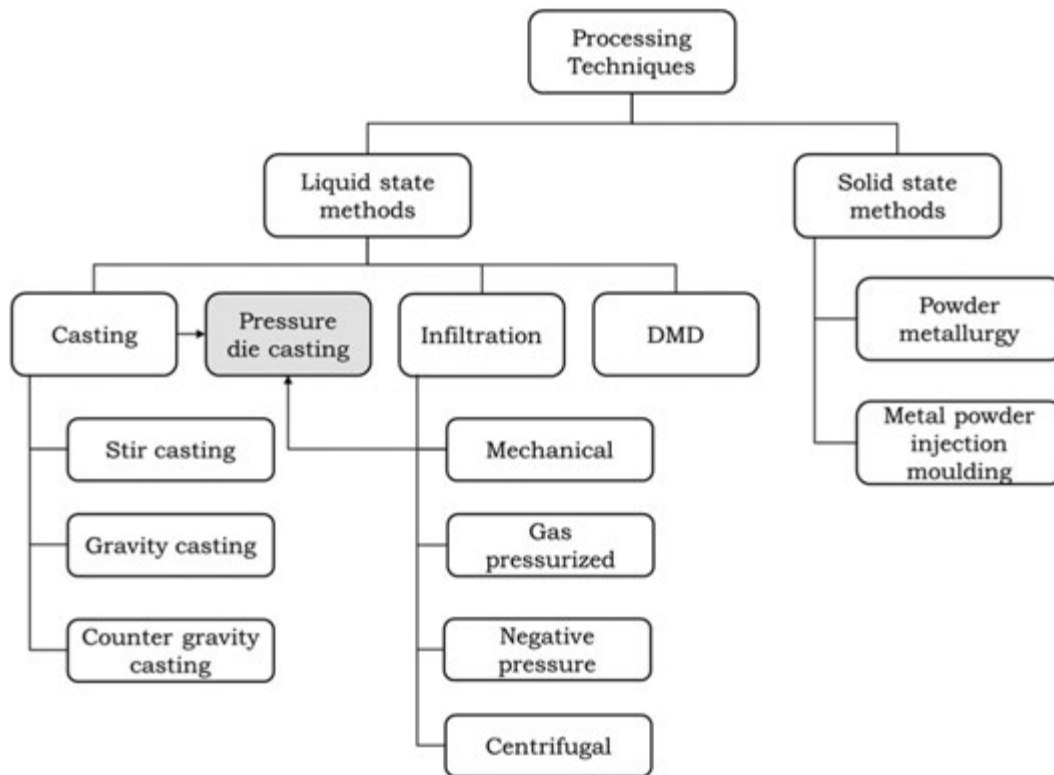


Fig. 6 Most common production methods of MMSFs.

the DMD technique. The main limitation of this technique is the difficulty of incorporating reinforcements with high volume fraction due to increased viscosity. This increase in viscosity leads to the heterogeneous distribution of reinforcements and difficulty in stirring. However, this limitation is not critical as the optimal volume fraction above which further addition of reinforcements won't affect the properties of the composites is already below the limits of this technique (Gupta and Wong, 2015).

Secondary Processing Techniques

Secondary processing like rolling, forging, and extrusion is used to further improve the properties of composite materials. However, in the case of syntactic foams, the mechanical and physical properties mainly depend on the matrix porosity and the native integrity of hollow particles. The strength and modulus of syntactic foams can be altered by varying the matrix microstructure. Due to the presence of a large amount of porosity, secondary processing of syntactic foams is not recommended. The properties of syntactic foams can be further enhanced by heat treatment (Gupta and Rohatgi, 2014).

Microstructure of MMSFs

Microstructure of the syntactic foams is found to vary based on the combination of matrix and alloy as well as on the potential application. Uniform distribution of particles in the matrix is the primary factor important for such MMSFs. A number of other microstructural concerns exist in studying syntactic foams, as discussed below.

A representative microstructure of Mg/cenosphere and AZ91D/cenosphere syntactic foams are shown in Fig. 8(a) and (b) respectively. The results of microstructural characterization in various studies (Daoud *et al.*, 2007; Rohatgi *et al.*, 2009; Huang *et al.*, 2010; Liu *et al.*, 2012) have reported the morphology and distribution of hollow particles and secondary phase particles of the composite foams as well as presence of some micro-voids at the particles/matrix interface. It has been observed that the amount of hollow particles is always less represented in the microstructure than the actual target value. This results from the replacement of hollow particles by the metal matrix due to pre-existing defects and cracks. Further, there will be intermetallic particles forming due to the reaction between the elements in the particle walls and matrix. Depending on the formation and distribution in the composites, the intermetallic particle layer formation can affect the mechanical properties of the syntactic foams. For example, in fly ash cenospheres reinforced ZC63 (Daoud *et al.*, 2007) and AZ91D (Rohatgi *et al.*, 2009; Huang *et al.*, 2010; Huang and Yu, 2011) alloys, MgAl_2O_4 , MgO and Mg_2Si are formed at the interface of the cenosphere and the matrix. In contrast, spheroidal Mg_2Si and $\text{Mg}_{17}\text{Al}_{12}$ are known to form in the matrix. Also, MgAl_2O_3 which may be generated,

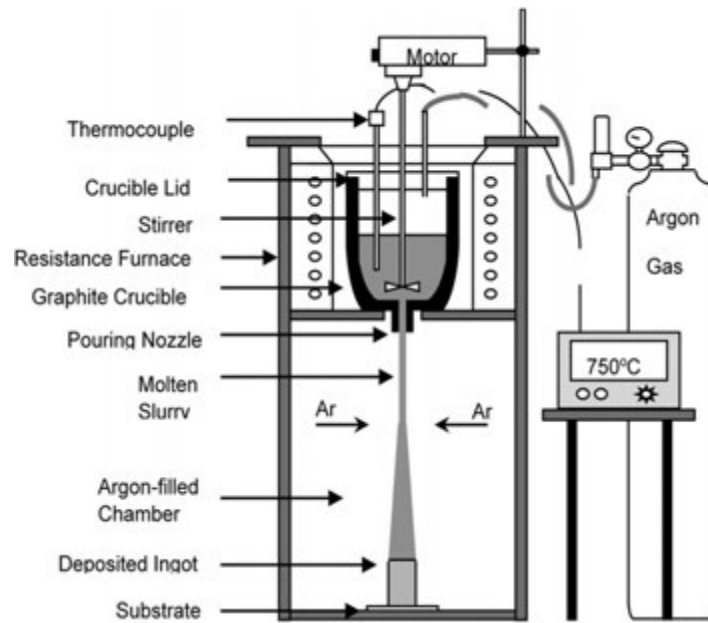


Fig. 7 Schematic diagram of disintegrated melt deposition technique. Reproduced from Gupta, M., *et al.*, 2017. An insight into high performance magnesium alloy/nano-metastable-syntactic composites. 17th Australian International Aerospace Congress: AIAC 2017, Engineers Australia, Royal Aeronautical Society.

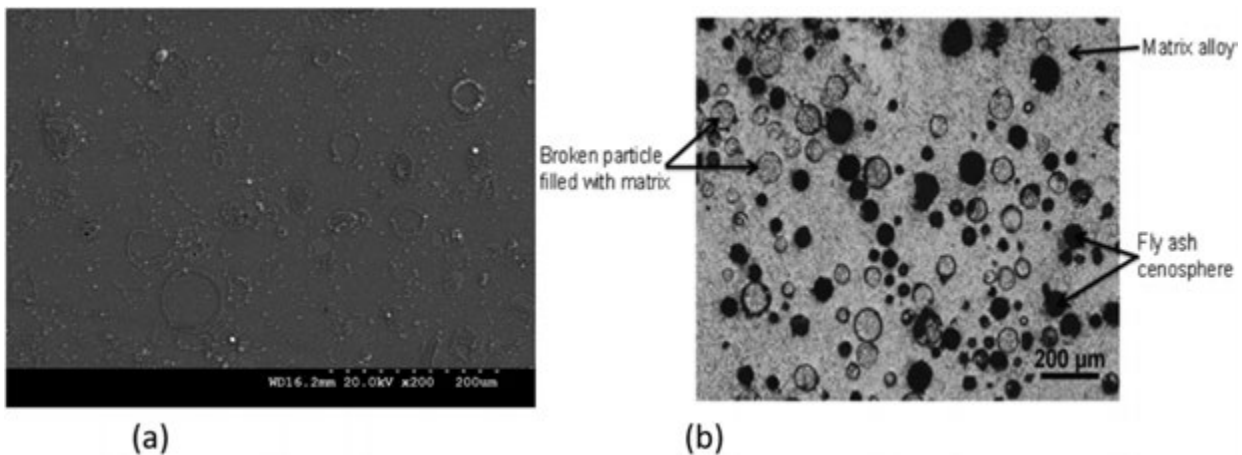


Fig. 8 Typical microstructure of (a) Mg/cenosphere and (b) AZ91D/cenosphere syntactic foams. Reproduced from Gupta, N., *et al.*, 2012. Magnesium matrix composite foams—density, mechanical properties, and applications. *Metals* 2 (3), 238–252.

further reacts with Mg and decomposes into MgO and Al (Gupta *et al.*, 2012). Fig. 9 shows the AZ91D microstructure with typical precipitates. Reaction products may be generated due to the interfacial reactions and may diffuse in the matrix in the inter-particle region. Some of the reaction products may accumulate at grain boundaries, which is undesirable. Al–Si alloy filled with hollow glass particle is found to have reactions with the SiO_2 present in the particles to produce MgAl_2O_4 .

Mechanical Properties

Compressive Properties

Due to their low density, high hydrostatic compressive strength, high damage tolerance, low moisture absorption coefficient, and good electromagnetic interference (EMI) shielding, and polymer syntactic foams have found wide applications as buoyancy modules for marine applications and underwater explorer vehicles (Gupta *et al.*, 2018). In such applications, these syntactic foams are often subjected to severe compressive loading, which can indicate areas where MMSFs can be useful. The properties of MMSFs can be tailored by a number of parameters such as type of the particle shell, shell wall thickness to diameter ratio, a combination of matrix alloy and particles, processing parameters, volume fraction, porosity, and heat treatment (Gupta *et al.*, 2012). All these parameters are found to

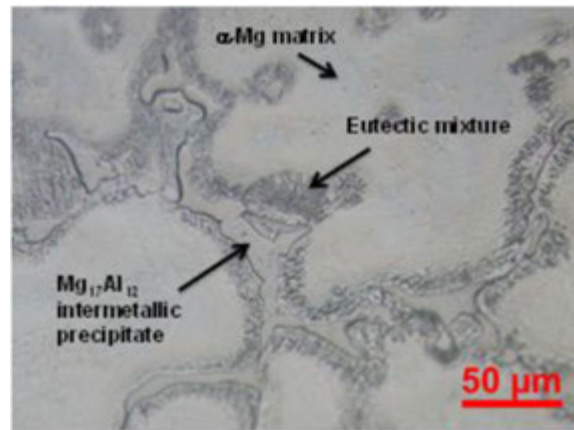


Fig. 9 AZ91 matrix microstructure showing precipitates. Reproduced from Gupta, N., *et al.*, 2012. Magnesium matrix composite foams—density, mechanical properties, and applications. *Metals* 2 (3), 238–252.

influence the mechanical properties as well as the density of the composite. The presence of controlled size porosity of a spherical shape with uniform distribution aids in providing high energy absorption under compression in syntactic foams (Rohatgi *et al.*, 2011). Therefore, syntactic foams are primarily designed to be used under compression. Incorporating stiff ceramic particles like cenospheres or glass microspheres in the syntactic foam structures helps obtain high modulus and strength as the particles act as load-bearing elements under compression (Gupta and Woldesenbet, 2004). As a result, most of the publications in the open literature have studied the compressive properties of MMSFs for a large number of metal matrices, including aluminum, magnesium, titanium, iron, Invar, zinc, and lead matrix syntactic foams reinforced with fly-ash cenospheres, glass microspheres and other engineered hollow particles such as alumina, silicon carbide, and boron carbide. Most of the mechanical data available for MMSFs are measured under quasi-static conditions, while the response of these foams to dynamic, tensile, and cyclic loading is limited to a subset of the materials available and provides the first indication of capabilities rather than comprehensive accounts of their performance. This section provides an overview and general references and trends regarding the most important properties of the MMSFs and comparison charts for material selection.

The red line illustrates a typical compressive stress-strain graph of a typical syntactic foam specimen in Fig. 10. The deformation characteristics of syntactic foams under compression are similar to those of conventional metal foams, and their stress-strain curves exhibit four distinct points, as shown in Fig. 10. For MMSFs, compressive strength and plateau stress are two properties that require attention. The compressive strength is defined as the peak stress after the linear elastic region in the stress-strain curve. At this peak, the failure of the hollow particle starts. The initial failure of hollow particles can be due to defects, such as cracks present in the hollow sphere walls. These relatively thin walled hollow spheres may have lower strength than other hollow spheres or localized stress concentrations resulting from factors like a group of closely spaced figures. Following the linear region appears the plateau region where the stress rises smoothly with increasing strain in the collapse region, indicating no strain hardening in the syntactic foam specimen during plastic deformation. The onset of the plateau region is governed by the fracture strength of the hollow particle shells and is realized once the stress is low enough for the bulk material to sustain a homogeneous compression. Depending on the particle wall thickness and volume fraction, the stress plateau can extend to over 50% densification strain depending on the total porosity in MMSFs. The compressive strength and plateau stress are important properties because the compressive strength is considered the maximum stress before the hollow particle fails, and the plateau stress related to the energy absorption capabilities of the MMSFs. In general, these values increase with the volume fraction of hollow particles.

Several possibilities exist for the superior compressive properties observed for syntactic foams when compared to conventional metal foams. Usually, pore collapse occurs at low applied compressive stresses in traditional foam of metal, whereas in syntactic foams, the pores are surrounded by stiff, strong ceramic walls, which impede their deformation and collapse during compressive loading, increasing the MMSF stiffness and strength (Fig. 11). The yielding behavior of MMSFs is influenced by a complex concurrence of processes such as the extent of hollow particle breakage, plastic deformation behavior of the matrix, and characteristics of the interface, including interfacial reaction and resultant interfacial bond strength, dislocations and load sharing between the reinforcement and the matrix. At lower volume fractions, the yield strength of the MMSFs is dominated by the strength of the reinforcing phase, whereas with increased filler loadings, both the matrix and the hollow particles contribute to strength. At higher volume fractions, the hollow particles contribute to the stress accommodation due to an increase in the matrix-particle interface resulting in higher yield strengths for MMSFs. Further, the possibility of controlling the uniform pore size and volume fraction of the porosity that can be reinforced into the metal matrix provides an opportunity to tailor the compressive properties of MMSFs to meet specific application requirements.

However, it should be noted that not all the MMSFs reported in the literature exhibit this true syntactic foam behavior, i.e., a horizontal, constant-stress plateau region extending over a significant strain range. Compression curves for several magnesium and iron syntactic foams reinforced with fly-ash cenospheres, glass microspheres and metal hollow spheres show a positive inclination at strains between initial yield and densification resulting from high work hardening of the matrix and fracture of particle causing compaction. The high reactivity of magnesium and processing challenges in synthesis of magnesium syntactic foams can often result in breakage of the hollow particles and infiltration of magnesium into the pore cavities resulting in compression behavior typically observed for MMCs reinforced with solid particulate fillers. Also, it has been reported that a critical threshold of 30 vol% porosity is required for MMSFs to

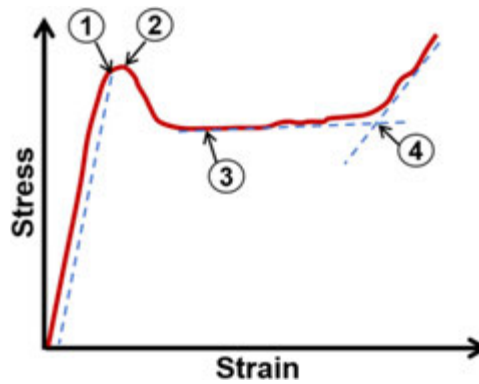


Fig. 10 Schematic representation of compressive stress-strain diagram of a typical MMSF specimen. The annotations in the graph refer to 1: yield strength, 2: compressive strength (peak strength), 3: plateau stress and 4: densification strain.

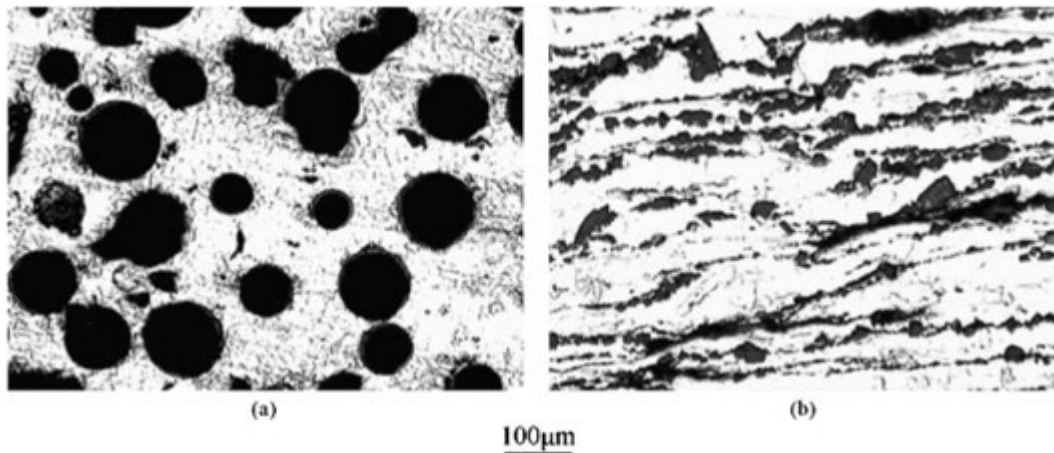


Fig. 11 Optical micrograph of longitudinal section of ZnAl22-25 vol% cenosphere syntactic foam after compression showing cenosphere fragments. Reproduced from Daoud, A., 2014. Zinc Matrix Syntactic and Composite Foams. Metal Matrix Syntactic Foams: Processing, Microstructure, Properties and Applications 137.

exhibit true syntactic foam behavior. Additionally, reinforcing hollow metal spheres to introduce porosity into a metallic matrix can result in similar overall behavior of the material as both the reinforcement and matrix are identical in composition, state, and relatively highly ductility. Further, the resulting compressive behavior is significantly affected by the interplay of the matrix and the hollow reinforcement. The complexity of this interplay has been illustrated by Lehmus *et al.* in a comparison study between identical volume percentages of cenospheres and S60HS glass microspheres reinforced into Fe99.7 matrix. It was observed that while the glass microspheres were found to cancel out ductility completely, cenosphere addition allowed the retention of some plasticity. Therefore, the development of special alloys to serve as matrix materials in syntactic foams should be critically looked at to obtain the best advantage of syntactic foams rather than incorporating microballoons in conventional monolithic alloy matrices. These alloys should be specially tailored to bond the microballoons by having favorable thermodynamics and kinetic for desired interfacial reactions.

Dynamic Compressive Properties

Many studies have investigated the dynamic compressive properties of MMSFs. Zhang and Zhao (2007) used the drop hammer test to study the low speed (4 m/s) impact response of Al matrix syntactic foams. Compared with static compression, the stress-strain curve of dynamic compression is different. It has oscillations at low strains because the impacting hammer experiences strong vertical vibrations when it hits the syntactic foam sample. Meanwhile, the impact peak strength is much higher than the compressive strength in static compression. (Altenaiji *et al.*, 2014) studied the characteristics of Al syntactic foams under drop weight impact and reported that impact peak strength is proportional to impact energy. Balch *et al.* (2005), Dou *et al.* (2007), Zhang *et al.* (2016, 2018) studied the impact response of Al matrix syntactic foams using Split-Hopkinson bars with high strain rates. The dynamic stress-strain curve is similar to static compression, but the compressive strength is much higher and strain rate dependent. Some of the results obtained from the literature for open- and closed-cell aluminum foams are compared with those for aluminum matrix syntactic foams in Fig. 12, where Fig. 12(a) is plotted with strain rate using normal axis and Fig. 12(b) is plotted with strain rate using log axis (Dou *et al.*, 2007; Luong *et al.*, 2011; Goel *et al.*, 2012, 2014; Rabiei and Garcia-Avila 2013; Zou *et al.*, 2013; Alvandi-Tabrizi and Rabiei 2014; Cox *et al.*, 2014; Santa Maria *et al.*, 2014).

These two modes allow more clear insight into high and low strain rate regions, respectively. The main observations from Fig. 12 are:

- Fig. 12(a) shows that most syntactic foam compositions are listed with over 100 MPa strength values, whereas foams containing gas porosity have strength values below 50 MPa for most compositions. This high strength is suited for load bearing applications. Syntactic foams have higher strength than open- and closed-cell foams at the same level of density. This observation is essential for structural applications.
- The strain rate sensitivity in aluminum-based foams is not very strong. It is known that face centred cubic metals are not strongly strain rate sensitive. Similar observations for magnesium and iron matrix syntactic foams may provide different results because of the inherent strain rate sensitivity of the matrix alloy.

The strain rate sensitivity is not limited only to mechanical properties. The failure mechanism of syntactic foams can also be strain rate dependent. As the strain rate is increased, the foam behavior transits from ductile to brittle. At sufficiently high strain rates, some of the foams fracture a minimal compressive strain. The characteristics of this type of failure include relatively less particle crushing, cracks in the specimen in the direction of compression, and suppression of shear effects.

Energy Absorption

Metal matrix syntactic foams have advantages in energy absorption because of the relatively higher plateau stress and extensive plateau regime. The former is mainly dependent upon the strengths of the metal matrix and microspheres and the volume ratio between the two. The latter relates to the densification strain, which is determined by the porosity of the syntactic foam. The specific energy absorption of CP Al matrix and Al 7075 matrix syntactic foams were about 39 and 49 J/g, respectively, which are significantly higher than those observed for unreinforced aluminum foams of similar density are comparable to steel foams fabricated by powder metallurgy (Balch *et al.*, 2005).

Weight Saving Potential of MMSFs

The weight saving potential of syntactic foams can be realized by understanding the relationship between syntactic foam density and mechanical properties. The compressive yield strength of ceramic reinforced syntactic foams normalized with the yield strength of the matrix material has been plotted for composite density in Fig. 13 to visualize the weight saving advantage. The data in the Fig. 13 represent Al, Mg, Ti, and Fe matrix syntactic foams and are taken from the available literature (Rohatgi *et al.*, 2006; Daoud *et al.*, 2007; Surappa, 2008; Daoud, 2009; Mondal *et al.*, 2009; Rohatgi *et al.*, 2009; Huang *et al.*, 2010; Xue *et al.*, 2010; Luong *et al.*, 2011; Peroni *et al.*, 2012; Luong *et al.*, 2013; Rocha Rivero *et al.*, 2013).

Some of the compressive properties presented here are extracted from the published graphs to the best possible accuracy. Also, the yield strength of the alloys that are needed to plot the Fig. 13 is taken from standard databases when it is not given in the same publication. It can be observed from Fig. 13 that the syntactic foam properties can be tailored over a wide range of strength values. The strength of several lightweight syntactic foams is equal to or close to the strength of the matrix material. Also, it can be noticed that the magnesium matrix syntactic foams have higher values of yield strength and maintain their superiority over most other types of syntactic foams. The aluminum matrix syntactic foams have yield strength values from about 30%–70% lower than that of magnesium matrix syntactic foams at comparable density. In contrast, iron syntactic foams have similar strength, their density is 2–3 times higher than the magnesium matrix syntactic foams. Weight saving can be achieved in load-bearing applications by replacing the aluminum and titanium matrix syntactic foams with magnesium matrix syntactic foams without compromising the strength. In general, higher density foams tend to have higher strength. Depending on the end requirements of the applications, appropriate material can be selected.

The novel behavior offered by MMSFs is higher specific properties. Further, the use of hollow particles such as fly ash reduces landfill sizes and minimizes environmental pollution. Further ease of processing makes them candidate materials for existing body frames of vehicles in the transportation sector, wherein energy absorption is of paramount importance. High energy absorption of the syntactic foams finds potential usage by foam-filling of the hollow parts of automobiles such as bumper systems and fenders, which may reduce injuries and damage due to impact loads (Fuganti *et al.*, 2000; Kovacik and Simancik, 2004). Further, these have been extensively used in defense applications like soldier helmets resulting in superior ballistic protection and impact resistance. Titanium and magnesium syntactic foams can be readily used as orthopedic implants in the biomedical regime, which acts as a load bearing element (Niemeyer, 1999). However, the potential of MMSFs in several other areas of applications is still not well explored.

MMSFs can be used in multifunctional applications, mainly in automotive, to serve as lightweight panels, absorb energy in crash situations and reduce acoustic emissions. They can also be used to build column structures due to their robustness and damage tolerance, making the failure less catastrophic. MMSFs can go a long way in the passive safety of the vehicles as they exhibit a reasonably long plateau range which helps in increased energy absorption. The automotive and indoor noise control is also a potential area where the feasibility of MMSFs can be explored. MMSFs can also be used for indoor sound absorption in places like auditoriums and cinemas. MMSFs with higher buckling and crippling resistance can be used to replace honeycomb structures in the aerospace turbines and also be used to replace existing load bearing structures in satellites and space vehicle landing pads (Banhart, 2001). If the central interest of material substitution is weight-saving, then perhaps there are several other cheaper materials that can be substituted other than MMSFs. However, good thermal properties, high specific strength, and energy absorption characteristics coupled with lightweight significantly increase the competitiveness of the MMSFs.

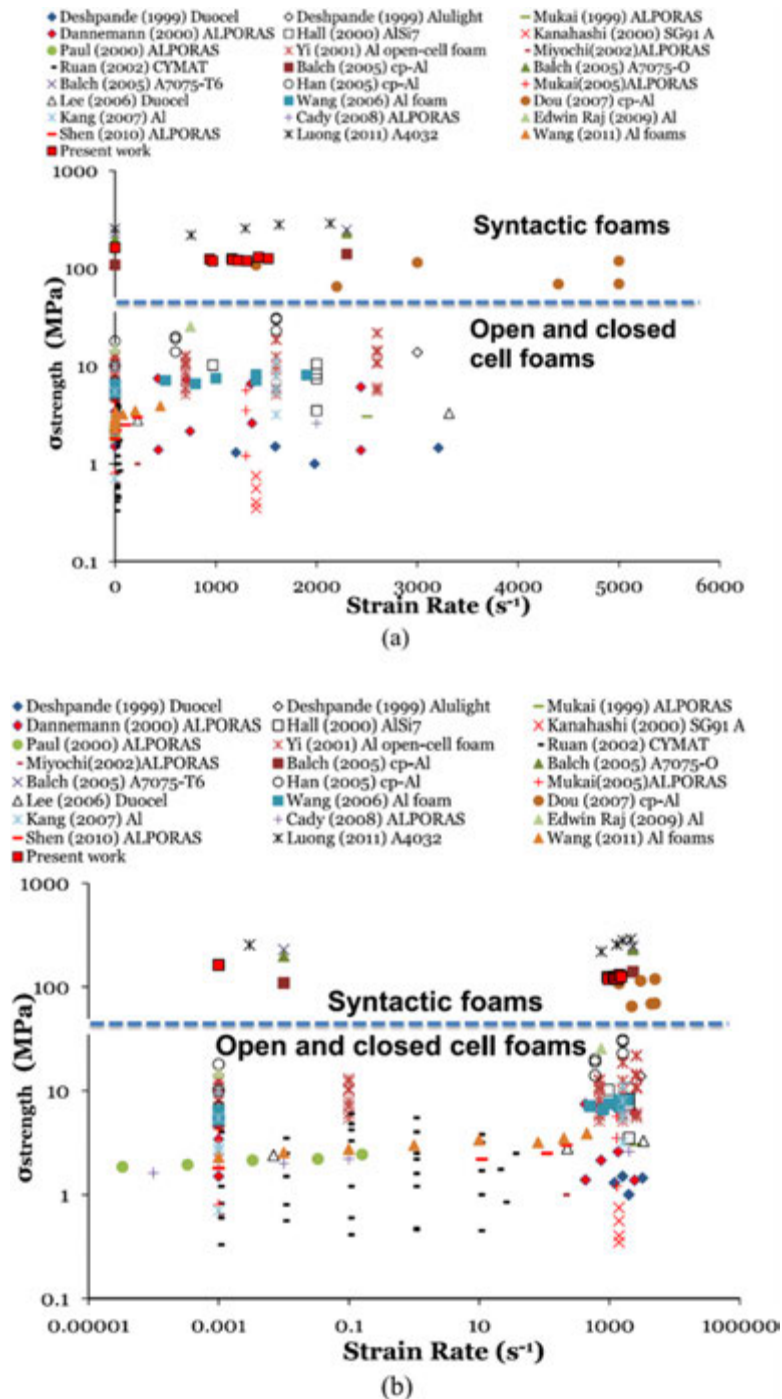


Fig. 12 Comparison of strength values for open and closed-cell aluminum foams containing gas porosity with those of aluminum matrix syntactic foams. The strain rate values are plotted on (a) normal axis and (b) log axis. In both cases the strength values are plotted on log axis. Reproduced from Gupta, N., Rohatgi, P.K., 2018. 4.15 Metal matrix syntactic foams.

Summary

In summary, this article presented the synthesis methods and mechanical properties of metal matrix composite syntactic foams (MMSFs). As the MMSFs are reinforced by hollow particles, they can also be considered as metal matrix composites. First, the constituents have been considered: the most commonly used matrices are Al alloys. Besides Mg, Zn, and Fe matrices are used, and work on Ti and Cu matrices can also be found in the literature. Subsequently, the filler materials have been summarized, emphasizing their properties, advantages, and disadvantages. Following that, the synthesis methods of the MMSFs have been grouped and discussed, emphasizing the potential of pressure die casting as a possible mass production method for MMSFs. In the

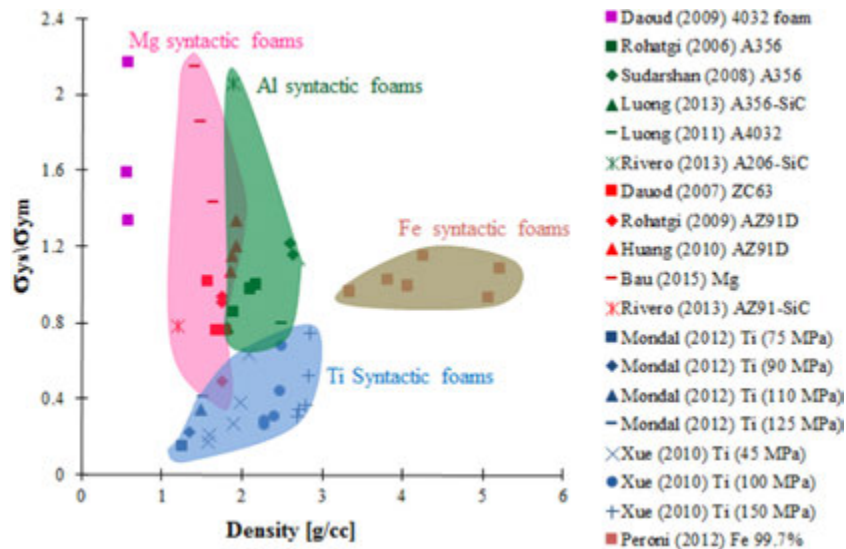


Fig. 13 Compressive yield strength of syntactic foams (σ_{ys}) normalized with the yield strength of the matrix material (σ_{ym}) plotted against density.

section about the microstructure of MMSFs, the primary imaging methods and basic inner structures have been described. Last but not least, a general insight into the mechanical properties of MMSFs has been given, discussing, in short, the quasi-static and dynamic properties of MMSFs, as well as their potential weight saving features and application areas, are highlighted.

References

- Altenaiji, M., Guan, Z.W., Cantwell, W.J., Zhao, Y., Schleyer, G.K., 2014. Characterisation of aluminum matrix syntactic foams under drop weight impact. *Materials & Design* 59, 296–302.
- Alvandi-Tabrizi, Y., Rabiei, A., 2014. Use of composite metal foam for improving absorption of collision forces. *Procedia Materials Science* 4, 377–382.
- Ashrith, H.S., *et al.*, 2019. Effect of wall thickness and cutting parameters on drilling of glass microballoon/epoxy syntactic foam composites. *Composite Structures* 211, 318–336.
- Balch, D.K., O'Dwyer, J.G., Davis, G.R., *et al.*, 2005. Plasticity and damage in aluminum syntactic foams deformed under dynamic and quasi-static conditions. *Materials Science and Engineering: A* 391 (1–2), 408–417.
- Banhart, J., 2001. Manufacture, characterisation and application of cellular metals and metal foams. *Progress in Materials Science* 46 (6), 559–632.
- Bharath, H.S., *et al.*, 2020. Mechanical behavior of 3D printed syntactic foam composites. *Composite Structures* 254, 112832.
- Bharath, H.S., *et al.*, 2021a. Flexural response of 3D printed sandwich composite. *Composite Structures* 263, 113732.
- Bharath, H.S., *et al.*, 2021b. Effect of axial compression on dynamic response of concurrently printed sandwich. *Composite Structures* 259, 112223.
- Bonthu, D., *et al.*, 2020. 3D printing of syntactic foam cored sandwich composite. *Composites Part C: Open Access* 3, 100068.
- Cox, J., Luong, D.D., Vasanth Chakravarthy, S., *et al.*, 2014. Dynamic and thermal properties of aluminum alloy A356/silicon carbide hollow particle syntactic foams. *Metals* 4 (4), 530–548.
- Daoud, A., *et al.*, 2007. Fabrication, microstructure and compressive behavior of ZC63 Mg–microballoon foam composites. *Composites Science and Technology* 67 (9), 1842–1853.
- Daoud, A., 2009. Effect of fly ash addition on the structure and compressive properties of 4032–fly ash particle composite foams. *Journal of Alloys and Compounds* 487 (1), 618–625.
- Daoud, A., 2014. Zinc Matrix Syntactic and Composite Foams. *Metal Matrix Syntactic Foams: Processing, Microstructure, Properties and Applications* 137.
- Doddamani, M., 2020. Dynamic mechanical analysis of 3D printed eco-friendly lightweight composite. *Composites Communications* 19, 177–181.
- Doddamani, M.R., *et al.*, 2011. Behavior of sandwich beams with functionally graded rubber core in three point bending. *Polymer Composites* 32 (10), 1541–1551.
- Dou, Z.Y., Jiang, L.T., Wu, G.H., *et al.*, 2007. High strain rate compression of cenosphere-pure aluminum syntactic foams. *Scripta Materialia* 57 (10), 945–948.
- Fuganti, A., *et al.*, 2000. Aluminum foam for automotive applications. *Advanced Engineering Materials* 2 (4), 200–204.
- Goel, M.D., Marco, P., George, S., *et al.*, 2012. Dynamic compression behavior of cenosphere aluminum alloy syntactic foam. *Materials & Design* 42, 418–423.
- Goel, M.D., Mondal, D.P., Yadav, M.S., Gupta, S.K., 2014. Effect of strain rate and relative density on compressive deformation behavior of aluminum cenosphere syntactic foam. *Materials Science and Engineering: A* 590, 406–415.
- Gupta, M., Wong, W., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.
- Gupta, N., *et al.*, 2012. Magnesium matrix composite foams—density, mechanical properties, and applications. *Metals* 2 (3), 238–252.
- Gupta, N., *et al.*, 2013. Reinforced Polymer Matrix Syntactic Foams: Effect of Nano and Micro-scale Reinforcement. Springer Science & Business Media.
- Gupta, N., *et al.*, 2018. Chapter 7 – Core materials for marine sandwich structures. In: Graham-Jones, J., Summerscales, J., Pemberton, R., *et al.* (Eds.), *Marine Composites: Design and Performance*. Elsevier Science, p. 187.
- Gupta, N., Rohatgi, P.K., 2014. *Metal Matrix Syntactic Foams: Processing, Microstructure, Properties and Applications*. Destech Publications Incorporated.
- Gupta, N., Woldesenbet, E., 2004. Experimental investigation on the effect of cenosphere radius ratio on the flatwise compressive properties of syntactic foams. *Composites Part A: Applied Science and Manufacturing* 35 (1), 103–111.
- Gupta, N., Doddamani, M., 2020. 3D printing of syntactic foams for marine applications. In: Lee, S.W. (Ed.), *Advances in Thick Section Composite and Sandwich Structures: An Anthology of ONR-sponsored Research*. Cham: Springer International Publishing, pp. 407–438.
- Gupta, N., Rohatgi, P.K., 2018. 4.15 Metal matrix syntactic foams.
- Hartmann, M., *et al.*, 1998. Fabrication and properties of syntactic magnesium foams. In: *Proceedings of MRS, Cambridge Univ Press*.
- Hrairi, M., *et al.*, 2009. Compaction of fly ash–aluminum alloy composites and evaluation of their mechanical and acoustic properties. *Advanced Powder Technology* 20 (6), 548–553.
- Huang, Z., Yu, S., 2011. Microstructure characterization on the formation of in situ Mg 2 Si and MgO reinforcements in AZ91D/Flyash composites. *Journal of Alloys and Compounds* 509 (2), 311–315.
- Huang, Z.-Q., *et al.*, 2010. Microstructures and compressive properties of AZ91D/fly-ash cenospheres composites. *Transactions of Nonferrous Metals Society of China* 20, s458–s462.

- Hyodo, T., *et al.*, 2005. Preparation of hollow alumina microspheres by microwave-induced plasma pyrolysis of atomized precursor solution. *Journal of the European Ceramic Society* 25 (16), 3563–3572.
- Jang, W.-Y., *et al.*, 2008. On the microstructure of open-cell foams and its effect on elastic properties. *International Journal of Solids and Structures* 45 (7–8), 1845–1875.
- Kanahashi, H., *et al.*, 2001. Experimental study for the improvement of crashworthiness in AZ91 magnesium foam controlling its microstructure. *Materials Science and Engineering: A* 308 (1), 283–287.
- Károly, Z., Szépvölgyi, J., 2003. Hollow alumina microspheres prepared by RF thermal plasma. *Powder Technology* 132 (2), 211–215.
- Kovacic, J., Simancik, F., 2004. Comparison of zinc and aluminum foam behavior. *Translations V.E. Rieckansky*.
- Liu, J., *et al.*, 2012. Microstructure and compressive property of in situ Mg 2 Si reinforced Mg-microballoon composites. *Journal of Alloys and Compounds* 537, 12–18.
- Luong, D.D., *et al.*, 2011. High strain rate compressive characterization of aluminum alloy/fly ash cenosphere composites. *Journal of the Minerals, Metals and Materials Society* 63 (2), 53–56.
- Luong, D.D., *et al.*, 2013. Development of high performance lightweight aluminum alloy/SiC hollow sphere syntactic foams and compressive characterization at quasi-static and high strain rates. *Journal of Alloys and Compounds* 550, 412–422.
- Manakari, V., *et al.*, 2015. Dry sliding wear of epoxy/cenosphere syntactic foams. *Tribology International* 92, 425–438.
- Manakari, V., *et al.*, 2016. Effects of hollow fly-ash particles on the properties of magnesium matrix syntactic foams: A review. *Materials Performance and Characterization* 5 (1), 116–131.
- Manakari, V., *et al.*, 2017. Enhancing the ignition, hardness and compressive response of magnesium by reinforcing with hollow glass microballoons. *Materials* 10 (9), 997.
- Manakari, V., *et al.*, 2019. Evaluation of wear resistance of magnesium/glass microballoon syntactic foams for engineering/biomedical applications. *Ceramics International* 45 (7, Part A), 9302–9305.
- Manakari, V., *et al.*, 2020. In-vitro degradation of hollow silica reinforced magnesium syntactic foams in different simulated body fluids for biomedical applications. *Metals* 10 (12), 1583.
- Matli, P.R., *et al.*, 2020a. A new method to lightweight magnesium using syntactic composite core. *Applied Sciences* 10 (14), 4773.
- Matli, P.R., *et al.*, 2020b. A novel method of light weighting aluminum using magnesium syntactic composite core. *Crystals* 10 (10), 917.
- Mondal, D., *et al.*, 2009. Cenosphere filled aluminum syntactic foam made through stir-casting technique. *Composites Part A: Applied Science and Manufacturing* 40 (3), 279–288.
- Montminy, M.D., *et al.*, 2004. The 3D structure of real polymer foams. *Journal of Colloid and Interface Science* 280 (1), 202–211.
- Mukai, T., *et al.*, 1999. Dynamic compressive behavior of an ultra-lightweight magnesium foam. *Scripta Materialia* 41 (4), 365–371.
- Niemeyer, M., 1999. *Proceedings of the DFG Symposium*, 11–12 November 1999. Bonn.
- Öchsner, A., Augustin, C., 2009. *Multifunctional Metallic Hollow Sphere Structures: Manufacturing, Properties and Application*, Engineering Materials, first ed. Berlin; Heidelberg: Springer-Verlag.
- Omar, M.Y., *et al.*, 2015. Syntactic foam core metal matrix sandwich composite under bending conditions. *Materials & Design* 86, 536–544.
- Padnuru Sripathy, A., *et al.*, 2021. Development of Lightweight Magnesium/Glass Micro Balloon Syntactic Foams Using Microwave Approach with Superior Thermal and Mechanical Properties. *Metals* 11 (5), 827.
- Parande, G., *et al.*, 2020. A study on the effect of low-cost eggshell reinforcement on the immersion, damping and mechanical properties of magnesium–zinc alloy. *Composites Part B: Engineering* 182, 107650.
- Patil, B., *et al.*, 2019a. Eco-friendly lightweight filament synthesis and mechanical characterization of additively manufactured closed cell foams. *Composites Science and Technology* 183, 107816.
- Patil, B., *et al.*, 2019b. Compressive behavior of fly ash based 3D printed syntactic foam composite. *Materials Letters* 254, 246–249.
- Peroni, L., *et al.*, 2012. Dynamic mechanical behavior of syntactic iron foams with glass microspheres. *Materials Science and Engineering: A* 552, 364–375.
- Prasadh, S., *et al.*, 2020. Hollow silica reinforced magnesium nanocomposites with enhanced mechanical and biological properties with computational modeling analysis for mandibular reconstruction. *International Journal of Oral Science* 12 (1), 1–11.
- Rabiei, A., Garcia-Avila, M., 2013. Effect of various parameters on properties of composite steel foams under variety of loading rates. *Materials Science and Engineering: A* 564, 539–547.
- Rajan, T., *et al.*, 2007. Fabrication and characterisation of Al–7Si–0.35 Mg/fly ash metal matrix composites processed by different stir casting routes. *Composites Science and Technology* 67 (15), 3369–3377.
- Rocha Rivero, G.A., *et al.*, 2013. Compressive properties of Al-A206/SiC and Mg-AZ91/SiC syntactic foams. *Journal of Materials Research* 28 (17), 2426–2435.
- Rohatgi, P., *et al.*, 1996. *Cast Aluminum, Fly Ash Composites for Engineering Applications*. American Foundrymen's Society, Inc. pp. 575–579.
- Rohatgi, P., *et al.*, 2006. Compressive characteristics of A356/fly ash cenosphere composites synthesized by pressure infiltration technique. *Composites Part A: Applied Science and Manufacturing* 37 (3), 430–437.
- Rohatgi, P., *et al.*, 2009. Microstructure and mechanical behavior of die casting AZ91D-Fly ash cenosphere composites. *Composites Part A: Applied Science and Manufacturing* 40 (6), 883–896.
- Rohatgi, P.K., *et al.*, 2011. The synthesis, compressive properties, and applications of metal matrix syntactic foams. *JOM Journal of the Minerals, Metals and Materials Society* 63 (2), 36–42.
- Sailesh, R., *et al.*, 2021. Acoustic behavior of 3D printed bio-degradable micro-perforated panels with varying perforation cross-sections. *Applied Acoustics* 174, 107769.
- Santa Maria, J.A., Schultz, B.F., Ferguson, J.B., Gupta, N., Rohatgi, P.K., 2014. Effect of hollow sphere size and size distribution on the quasi-static and high strain rate compressive properties of Al-A380–Al 2 O 3 syntactic foams. *Journal of Materials Science* 49 (3), 1267–1278.
- Shahapurkar, K., *et al.*, 2019. Effect of cenosphere filler surface treatment on the erosion behavior of epoxy matrix syntactic foams. *Polymer Composites* 40 (6), 2109–2118.
- Singh, A.K., *et al.*, 2019. Additive manufacturing of three-phase syntactic foams containing glass microballoons and air pores. *JOM* 71 (4), 1520–1527.
- Solórzano, E., *et al.*, 2008. Thermal conductivity of AZ91 magnesium integral foams measured by the Transient Plane Source method. *Materials Letters* 62 (24), 3960–3962.
- Surappa, M., 2008. Synthesis of fly ash particle reinforced A356 Al composites and their characterization. *Materials Science and Engineering: A* 480 (1), 117–124.
- Tao, X., *et al.*, 2009. Al matrix syntactic foam fabricated with bimodal ceramic microspheres. *Materials & Design* 30 (7), 2732–2736.
- Thornby, J., *et al.*, 2019. Indentation-based characterization of creep and hardness behavior of magnesium carbon nanotube nanocomposites at room temperature. *SN Applied Sciences* 1 (7), 1–12.
- Thornby, J., *et al.*, 2021. Micromechanics and indentation creep of magnesium carbon nanotube nanocomposites: 298 K–573 K. *Materials Science and Engineering: A* 801, 140418.
- Waddar, S., *et al.*, 2018. Snap-through buckling of fly ash cenosphere/epoxy syntactic foams under thermal environment. *Thin-Walled Structures* 131, 417–427.
- Waddar, S., *et al.*, 2019. Buckling and vibration behavior of syntactic foam core sandwich beam with natural fiber composite facings under axial compressive loads. *Composites Part B: Engineering* 175, 107133.
- Watanabe, M., *et al.*, 2007. Nano-sized Ni particles on hollow alumina ball: Catalysts for hydrogen production. *Applied Catalysis B: Environmental* 71 (3), 237–245.
- Wen, C., *et al.*, 2004. Compressibility of porous magnesium foam: Dependency on porosity and pore size. *Materials Letters* 58 (3), 357–360.
- Wu, J., *et al.*, 2019. Porous polymers as multifunctional material platforms toward task-specific applications. *Advanced Materials* 31 (4), 1802922.
- Xue, X., *et al.*, 2010. *Mechanical and biological properties of titanium syntactic foams*, Minerals, Metals and Materials Society/AIME, 420 Commonwealth Dr., P. O. Box 430, Warrendale, PA 15086, USA.
- Zhang, L., Zhao, Y., 2007. Mechanical response of Al matrix syntactic foams produced by pressure infiltration casting. *Journal of Composite Materials* 41 (17), 2105–2117.
- Zhang, Q., Yingfei, L., Haitao, C., Jing, C., Gaohui, W., 2018. Quasi-static and dynamic compression behavior of glass cenospheres/5A03 syntactic foam and its sandwich structure. *Composite Structures* 183, 499–509.
- Zhang, B., Yingfei, L., Shuo, L., Dongxian, Z., Gaohui, W., 2016. Quasi-static and high strain rates compressive behavior of aluminum matrix syntactic foams. *Composites Part B: Engineering* 98, 288–296.
- Zou, L.C., Zhang, Q., Pang, B.J., *et al.*, 2013. Dynamic compressive behavior of aluminum matrix syntactic foam and its multilayer structure. *Materials & Design* 45, 555–560.

Insight Into Layered Metal Matrix Composites

Akshay Padnuru Sripathy and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Laminated metal composites (LMCs) are the materials formed by bonding stacked layers of two or more materials. LMCs are one of the oldest known technologies to mankind. The Japanese and Damascus swords, Indonesian Kris (Lesuer *et al.*, 1996; Forster *et al.*, 1993) etc., are few examples from the past which are made out of laminated metal composites. LMCs have gained greater research interest due to their superior mechanical strength, ductility, and corrosion resistance (Chen *et al.*, 2020; Ellis and Lewandowski, 1994). LMCs typically have one soft/ductile material coupled with hard/brittle material stacked one above the other to realize desired strength, ductility and toughness. LMCs can be broadly classified into five sub categories based on the type of materials used as: (1) metal – metal laminates, (2) metal-intermetallic laminates (MIL), (3) metal – ceramic laminates, (4) fiber-metal laminates and (5) metal-metal matrix composite laminates. Fig. 1 shows classification of LMCs. The LMCs are also called metal based laminated materials. Further sections of the article focus mostly on metal-metal matrix composite laminates.

LMCs are also classified based on the stacking sequence, as angle and cross-ply laminates which can be of symmetric, antisymmetric or balanced (Kaw, 2006). Based on number of layers, LMCs are also identified as bi-layer, tri-layered and multi-layered materials.

Metal – Metal Matrix Composite Laminates

Metal-Metal Matrix Composite laminates are a type of laminated metal composites with at least one of the material layers as metal matrix composite. Generally, MMCs used in Metal – MMC Laminate are brittle in nature and pose high strength with lack of ductility. On the other hand, the metal layer used can be pure metal or an alloy with higher ductility and toughness. Metal – MMC laminates are also called by various names which include Layered Metal Matrix Composites (LMMCs), Laminated metal matrix composites (LMMCs) and Metal Matrix Composite Sandwich Panel (Ko and Jackson, 1993).

The Metal – MMC laminates or Layered Metal Matrix Composites (LMMCs) can be further classified as Similar Metal – Metal Matrix Composite Laminates and Dissimilar Metal – Metal Matrix Composite Laminates. Similar Metal-MMC laminates are those, where monolithic MMCs are coupled with monolithic metals or alloys which are similar to the matrix of MMCs. For instance, Ti – (TiB + La₂O₃)/Ti (Duan *et al.*, 2016), Ti – TiB_w/Ti (Liu *et al.*, 2014a), Al6063 – (TiB₂ + TiC)_p/Al6063 (Chen *et al.*, 2020), AA1050 – SiC_p/AA6061 (Hosseini Monazzah *et al.*, 2014) are few titanium and aluminum based similar Metal-MMCs laminates. Dissimilar Metal – MMC laminates are those where monolithic MMCs are coupled with monolithic metal or alloys which is different from the matrix of MMCs. Ti – SiC_p/Al (Fan *et al.*, 2017), Al5083 – TiC/Cu (Tomida *et al.*, 2001), Mg – SiC/Al (Syn *et al.*, 1996) are few examples of dissimilar metal-MMC laminates.

Microscopically, MMCs consist of metal matrix with dispersed particle or fiber reinforcements. In general, introducing precipitates, particle or fiber reinforcements in metal matrix increases strength of the metal with the expense of ductility and plasticity. Similarly, MMCs often show characteristics of high strength and stiffness with low ductility (Duan *et al.*, 2016; Gao *et al.*, 2020;

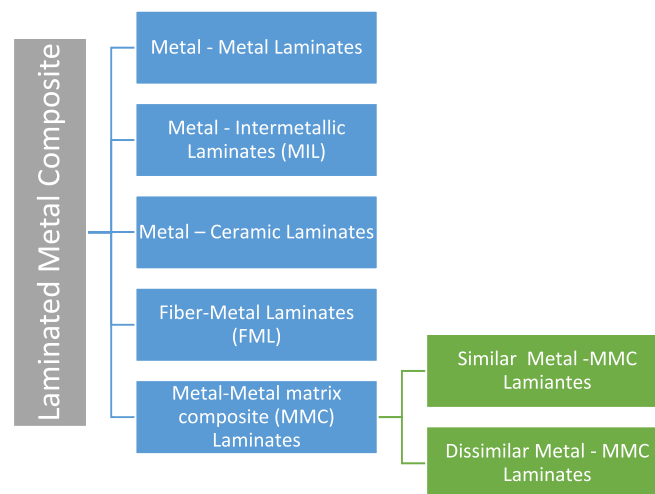


Fig. 1 Classifications of laminated metal composites.

Table 1 List of properties of MMCs and LMMCs

	Material	TYS (MPa)	UTS (MPa)	Elongation (%)	
MMC	5 vol% (TiB ₂ + TiC)p/Al	111.2	152.1	10.5	Chen <i>et al.</i> (2020)
	5 vol% TiB _w /Ti	656 ± 6	720 ± 7	7.5 ± 0.2	Liu <i>et al.</i> (2014a)
	10 vol% SiCp/Al	–	156 ± 11	11.8 ± 1.2	Fan <i>et al.</i> (2017)
	5 vol% TiB _w /Ti	656	720	7.5	Liu <i>et al.</i> (2013)
	8 vol% TiB _w /Ti	672 ± 6	832 ± 7	5.9 ± 0.2	Liu <i>et al.</i> (2014b)
LMMC	Al6063–5 vol% (TiB ₂ + TiC)p/Al	247.4	255.8	11.6	Chen <i>et al.</i> (2020)
	Ti-5 vol% TiB _w /Ti ^a	541 ± 6	638 ± 7	19 ± 0.3	Liu <i>et al.</i> (2014a)
	Ti-10 vol% SiCp/Al	–	363 ± 25	24.5 ± 1.5	Fan <i>et al.</i> (2017)
	Ti-5 vol% TiB _w /Ti ^b	496	617	20.5	Liu <i>et al.</i> (2013)
	Ti-8 vol% TiB _w /Ti	552 ± 7	689 ± 7	14.1 ± 0.3	Liu <i>et al.</i> (2014b)

^aDiffusion welding.^bReaction hot pressing.

Liu *et al.*, 2014b; Monazzah *et al.*, 2013), plasticity (Duan *et al.*, 2016), toughness (Gao *et al.*, 2020), and low damage tolerance (Monazzah *et al.*, 2013). Lack of ductility and damage tolerance of MMCs can be attributed to incompatible deformation between matrix and reinforcements owing to localized strain resulting in easy crack initiation and crack propagation (Fan *et al.*, 2017). Although MMCs are used in aerospace industry, automotive industry, military, sports equipment, widespread applications are limited due to their low ductility and toughness (Gao *et al.*, 2020; Hassan *et al.*, 2004a).

On the other hand, laminate structures are an effective and useful way to improve toughness of the material (Ellis and Lewandowski, 1994; Wang *et al.*, 2018; Wu *et al.*, 2016). Miracle *et al.* (2001) reported 79% improvement in fracture toughness in LMMCs compared to its MMC counterpart. Table 1 shows the list of properties of MMCs and its LMMCs. These laminate system abets effective harnessing of superior ductility and toughness characteristic of softer/ductile material and superior strength characteristic of brittle/hard material, resulting in laminated composite with good ductility, toughness and strength (Liu *et al.*, 2014b). Miracle *et al.* (2001) termed LMMCs as smart structures. In scenarios where development of MMCs are associated with the balancing strength and ductility, LMMCs can be of great help in achieving desired properties (Hassan *et al.*, 2004a; Wang *et al.*, 2018; Wu *et al.*, 2016; Partridge *et al.*, 1996). In addition, LMMCs can also be used to achieve superior tribological properties of alloy materials. Tomida *et al.* (2001), clad aluminum alloy 5083 with thick layer of TiC/Cu metal matrix composite and achieved superior wear resistance which was six times harder than Al alloy substrate.

Processing of LMMCs

There are various processing techniques by which LMMCs can be manufactured. Few technologies from the current known methods to process laminated metal composites can be utilized to synthesize LMMCs. Like all other materials, LMMCs also show variation in properties based on manufacturing technique. Table 1 shows various mechanical properties of the LMMC materials synthesized using two different techniques. A comprehensive study on the manufacturing processes of laminated metal composite is published by Lesuer *et al.* (1996). From the literatures available, it can be inferred that not all the process mentioned in article by Lesuer *et al.* (1996) are utilized in manufacturing LMMCs. However, few processing techniques are utilized in developing LMMCs by various researchers. This section attempts to consolidate the various processing techniques used in fabrication of LMMCs and chart of the same is shown in Fig. 2.

Bonding

Bonding is a process of establishing an interatomic bond between layers of material by means of application of temperature, pressure, chemical reaction, diffusion or by use of adhesive agents. In context of LMMCs, the two layers are metal and metal matrix composite. There are various types of bonding techniques that can be employed in developing LMMCs. Based on the published research work, the bonding techniques are classified into four categories; adhesive bonding, roll bonding, diffusion bonding and reactive hot pressing. Surface treatment, bonding temperature & pressure, diffusion, chemical reactions, adhesive agents properties plays major role in mechanical and physical properties of the laminates (Lesuer *et al.*, 1996).

Adhesive bonding

Adhesive bonding is where the layer of metal and MMC are bonded at their interface by an adhesive. ARALL (Aramid Reinforced Aluminum Laminates) and GLARE (Glass Reinforced) are well known Fiber metal laminates which form the entire top of the fuselage of Airbus A3XX (Hassan *et al.*, 2004a). Successful developments of various metal laminates via adhesive bonding, persuaded researchers to investigate adhesive bonding technique to develop of metal – MMCs laminates.

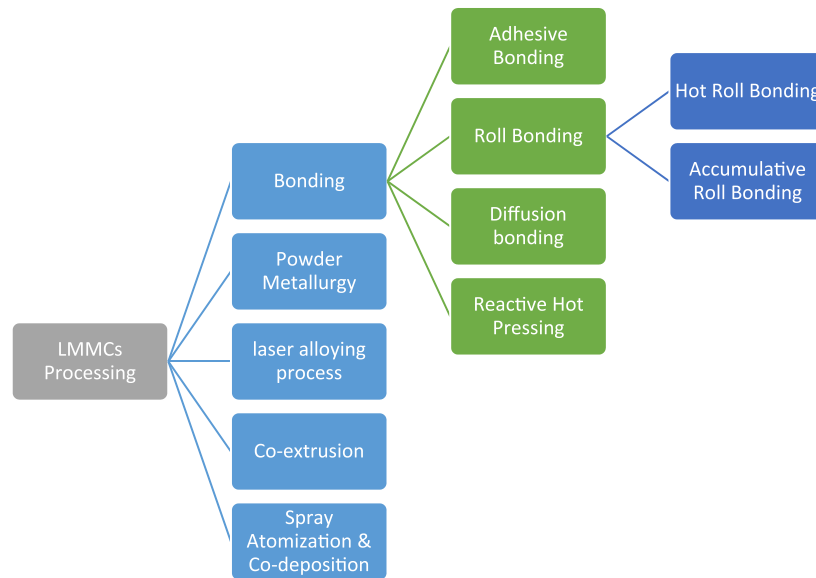


Fig. 2 Various processing techniques of LMMCs.

Osman *et al.* (2008) developed aluminum based LMMCs 7093-SiC_p/7093 using epoxy as adhesive. The adhesive bonding technique displayed a strong interfacial bonding exhibiting least delamination compared to other roll bonded laminate samples (Osman *et al.*, 2008). Following the attempts made by Osman *et al.* (2008), Hassan *et al.* (2004a) also fabricated AF163–2K (3M Co) epoxy bonded aluminum based LMMCs 2080- SiC_p/2080. The monolithic aluminum and MMCs layers were degreased and etched with nitric acid followed by smearing of ABR127 primer prior to application of epoxy.

Roll bonding

Roll bonding is a process of bonding two layers of metals at their interface using rolling metal forming process as primary means to apply pressure together with heating. Depending on the temperature and plastic deformation parameters, roll bonding can be sub categorized into hot rolling, cold rolling and accumulative rolling bonding. Hot rolling and accumulative roll bonding techniques are predominantly utilized in developing LMMCs. The roll bonding process is used to manufacture plate or sheet form of LMMCs (Lesuer *et al.*, 1996).

Hot roll bonding

Hot roll bonding is commonly utilized roll bonding technique in fabricating LMMCs. Hot roll bonding is roll bonding process with application of higher temperature typically above recrystallization temperature. Fig. 3 shows the schematic diagram of roll bonding process. However, the strain in the material is lesser than accumulative roll bonding.

Hosseini Monazzah *et al.* (2014) developed aluminum based LMMCs AA1050 - SiC_p/AA6061 using hot roll bonding. In the process, the layers were heated to 475°C and at the end of five consecutive rolling, total true strain imposed on the material was 63%. Similarly, Osman *et al.* (2008) also fabricated aluminum based LMMCs 7093 - SiC_p/7093 via hot roll bonding at high temperature and realized approx. 60% thickness reduction.

Accumulative roll bonding (ARB)

Accumulative roll bonding (ARB) is a severe plastic deformation technique involving repeated rolling processes to form bonding between two materials. Typical cycle of an ARB process involves surface preparation by degreasing mechanically and chemically, stacking, rolling and cutting (Tsuji *et al.*, 1999). The process is repeated to accumulate strain in the materials there by realizing stronger bond between the layers and while realizing ultra-fine grains (Tsuji *et al.*, 1999). The process is carried under elevated temperature for better joining and workability of materials (Tsuji *et al.*, 1999). However, the operating temperature is generally maintained below recrystallization temperature, as very high temperatures result in recrystallization and cancellation of accumulated strain (Tsuji *et al.*, 1999; Saito *et al.*, 1999). Fig. 4 shows various steps of ARB process.

Chen *et al.* (2020) successfully fabricated aluminum based LMMC Al6063-(TiB₂ + TiC)_p/Al up to 3 cycles and reported strong bonding between the monolithic Al alloy and Al MMC. The developed aluminum based LMMCs exhibited superior tensile strength and ductility than (TiB₂ + TiC)_p/Al. The tensile properties of this system are listed in the Table 1.

Diffusion bonding

As defined by Everett (1991), diffusion bonding is a solid-state welding technique which can be used to join similar or dissimilar metals. An elaborate definition of diffusion bonding can also be found in the article by Shirzadi (2008). Diffusion welding,

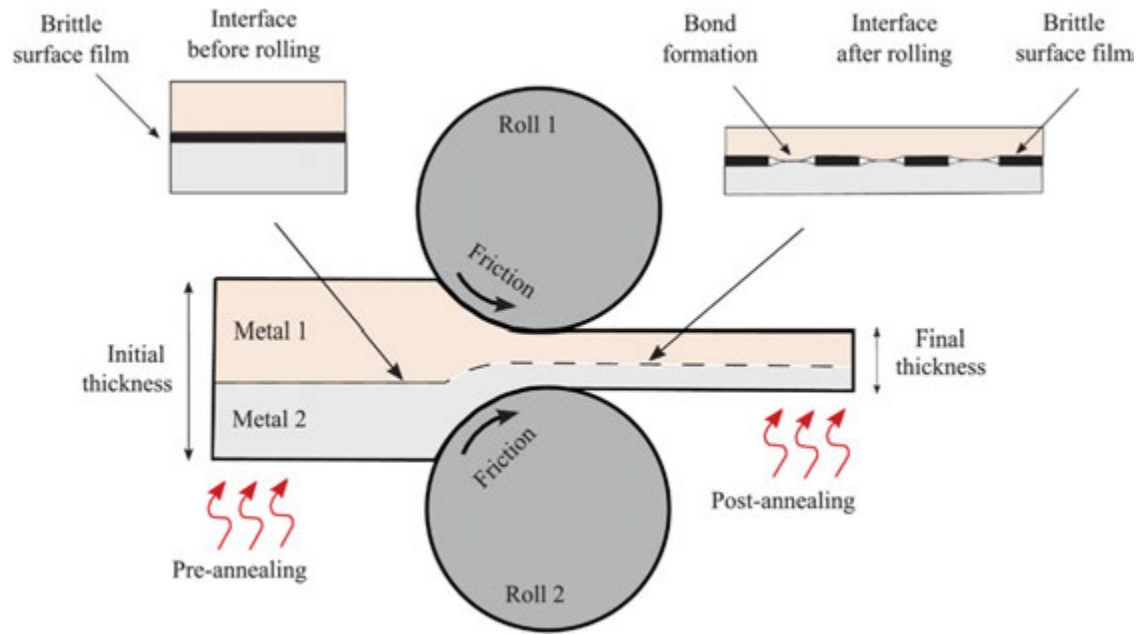


Fig. 3 Schematic diagram showing roll bonding process. Reproduced from Khaledi, K., Rezaei, S., Wulfinghoff, S., Reese, S., 2019. Modeling of joining by plastic deformation using a bonding interface finite element. *International Journal of Solids and Structures* 160, 68–79. doi:10.1016/j.ijsolstr.2018.10.014.

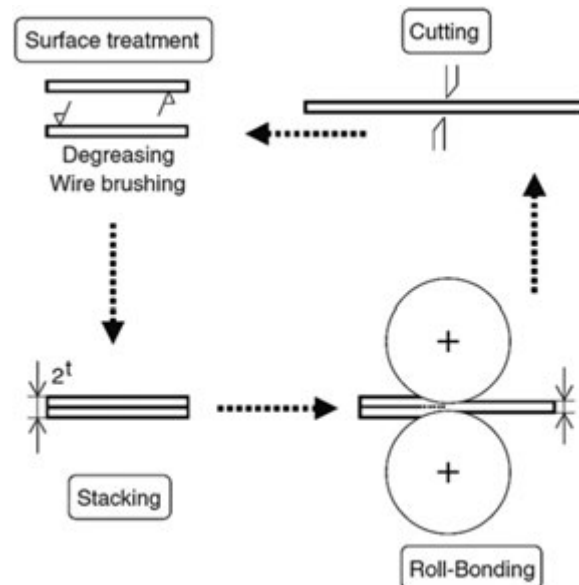


Fig. 4 Schematic representation of ARB process. Reproduced from Ghalehbandi, S.M., Malaki, M., Gupta, M., 2019. Accumulative roll bonding – A review. *Applied Sciences* 9 (17), 3627. doi:10.3390/app9173627.

isostatic bonding, hot press bonding, auto-vacuum welding and thermo-compression welding are few types of diffusion bonding (Shirzadi, 2008). A deeper understanding of diffusion bonding can be attained from articles elsewhere (Everett, 1991; Shirzadi, 2008; Lee, 2012; Kazakov, 1985a,b). Fig. 5 represents a typical diffusion bonding technique used for developing LMMCs.

Hot pressing variant is most commonly reported diffusion bonding technique in synthesizing LMMCs. In an overview, diffusion bonding between two layers of metals is a result of diffusion of atoms across an interface (Lee, 2012). At first, the metal layers are cleaned from contaminations, oil and dirt chemically or mechanically. Layers of metal and MMC are stacked to form green compact. The compact is then heated under vacuum atmosphere and pressure for desirable period. In general, diffusion bonding process is carried at temperature 50%–70% of melting temperature, vacuum of 10^{-3} – 10^{-5} mbar or inert atmosphere and pressure (Shirzadi, 2008). The interfacial bonding of layers can be controlled by varying temperature, pressure and time.

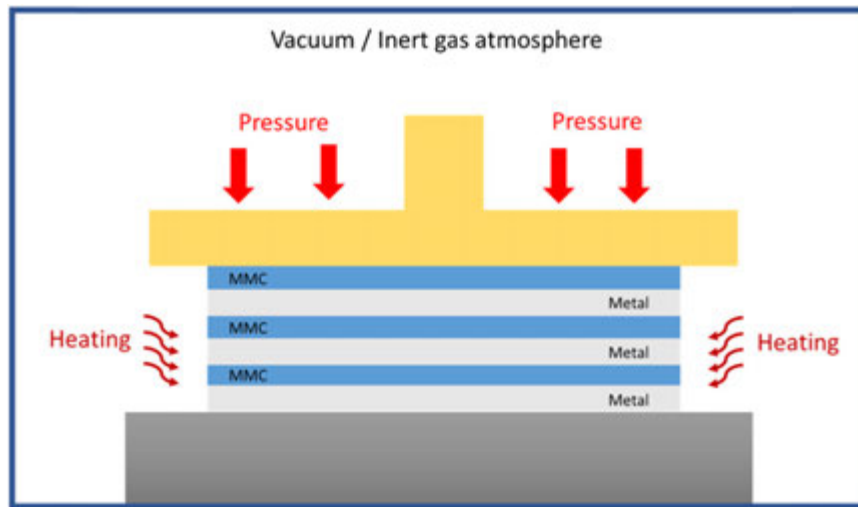


Fig. 5 Schematic diagram showing diffusion bonding technique.

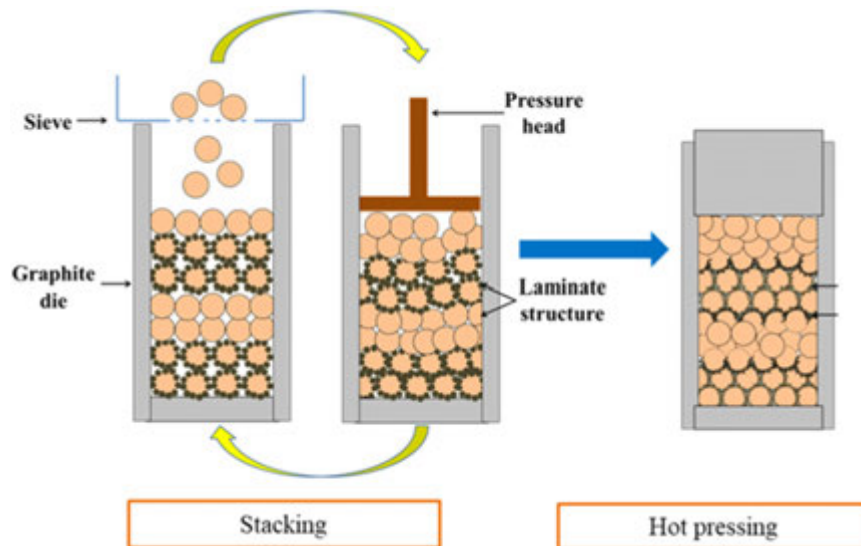


Fig. 6 Schematic diagram showing reactive hot pressing process to produce LMMCs. Reproduced from Wang, S., Huang, L., An, Q., Geng, L., Liu, B., 2018. Dramatically enhanced impact toughness of two-scale laminate-network structured composites. *Materials & Design* 140, 163–171. doi:10.1016/j.matdes.2017.11.067.

Liu *et al.* (2014a,b) developed titanium based LMMCs sheets Ti-TiB_w/Ti via diffusion bonding technique under vacuum (10^{-2}). During the process, the sheets were held at 1200°C under 25 MPa pressure to develop strong interfacial bond. Smith *et al.* (1997) also successfully developed Ti based LMMCs using diffusion bonding method. Syn *et al.* (1996, 1994) developed Mg-9%Li alloy-25 vol% SiCp/Al6090 and Al5182-25 vol% SiCp/Al6090 laminates via diffusion bonding using argon gas environment.

Reactive hot pressing (RHP)

Reactive hot pressing is a process by which simultaneous chemical reaction and densification of powders takes place under the application of pressure and temperature (Chaklader, 1965; Qiang *et al.*, 2008). Since the temperature in the process is less than the sintering process and the densification of powders occur concurrently, the reactive hot pressing is considered economical, also it can be an alternative for low temperature sintering process (Qiang *et al.*, 2008; Wu *et al.*, 2008). It is noteworthy that “reactive hot pressing” is another ceramic processing technique like sintering, hot pressing or pressure fabrication (Chaklader, 1965). The RHP is extensively used to fabricate ceramic based composites (Wu *et al.*, 2008; Zhang *et al.*, 2009; Kannan and Rangaraj, 2018). A schematic diagram representing reaction hot pressing is shown in Fig. 6.

Liu *et al.* (2013, 2014c) developed titanium based LMMC Ti-TiBw/Ti by reaction hot pressing. The TiBw/Ti powders were placed on top of Ti sheets and hot pressed in vacuum (10^{-2}) at 1200°C and 25 MPa pressure for 40 min Wang *et al.* (2018) also developed titanium based LMMC Ti-TiBw/Ti via reaction hot pressing.

Powder Metallurgy

Powder metallurgy is a versatile manufacturing technique which can produce large variety of materials like alloys, composites, laminates etc. The various stages of powder metallurgy are shown in Fig. 7. The powder metallurgy utilized in developing LMMCs follows the same procedure as that of the conventional technique with a modification in the process of powder consolidation. While the powders are poured into die for powder compacting, alternative layers of the metal and MMCs are poured to form stacked layers of Metal and MMCs. Layer thickness is estimated by the mass of the powder as per Eq. (1) where A is the cross sectional area of the die, H is the height of the powder layers i.e. metal/Alloy or MMC and ρ is the density of the material.

$$\text{Mass} = A \times H \times \rho \quad (1)$$

While developing LMMCs, sintering stage in powder metallurgy might lead to various predicaments like porosity, cracking, bending, delamination and deformation in the layers due to thermal mismatch between the materials (Prikhodko *et al.*, 2020). Often the LMMCs developed through powder metallurgy process are subjected to secondary processing for further densification, to induce strain or to achieve various mechanical properties (Prikhodko *et al.*, 2020).

Duan *et al.* (2016) synthesized Ti - (TiB + La_2O_3)/Ti LMMCs using powder metallurgy followed by hot rolling to reduce porosity, grain refinement and to improved relative density from 95% to 100%.

Laser Surface Alloying Process

Laser surface alloying (LSA) is a type of laser surface treatment process, capable of producing coating, thereby enhancing resistance to corrosion, erosion, wear, oxidation or fatigue (Wong *et al.*, 2012). As defined by Wong *et al.* (2012) Laser surface alloying is a technique that involves melting of a pre-/co-deposited layer of alloying material(s) along with a part of the underlying substrate to form an alloyed zone (AZ) confined to a shallow depth from the surface within a very short interaction time. Fig. 8 shows a variant of laser alloying processing setup.

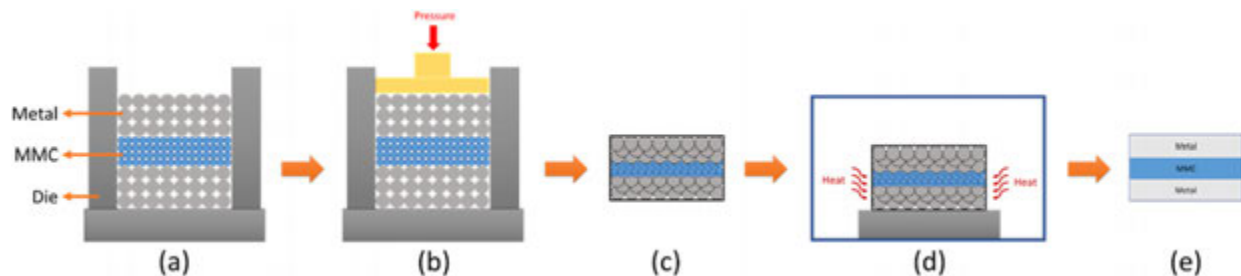


Fig. 7 Schematic diagram showing powder metallurgy process to process LMMCs (a) Metal and MMC powder stacking (b) Powder compacting (c) Billet / green compact (d) Sintering (e) Synthesized LMMC.

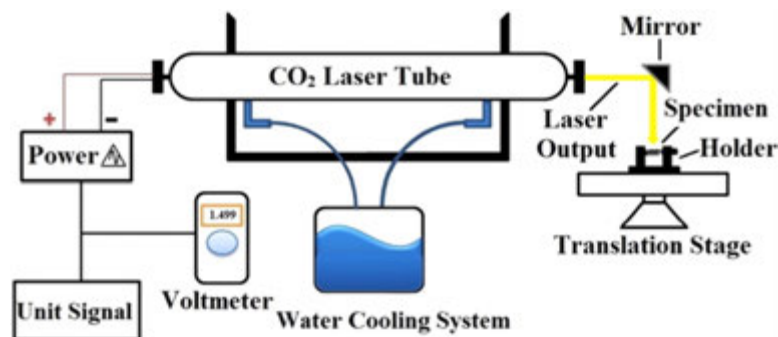


Fig. 8 Schematic diagram of laser surface alloying process. Reproduced from Salim, A.A., Bidin, N., Islam, S., 2017. Low power CO_2 laser modified iron/nickel alloyed pure aluminum surface: Evaluation of structural and mechanical properties. Surface and Coatings Technology 315, 24–31. doi:10.1016/j.surfcoat.2017.02.016.

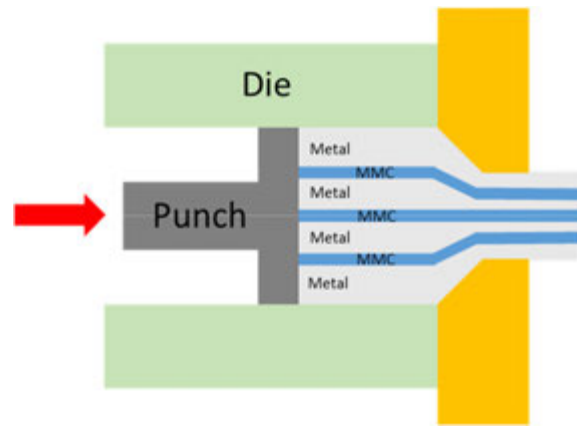


Fig. 9 Schematic representation of Co-Extrusion process.

In LSA, the coating materials in the form of powders are pre placed in the cleaned, degreased substrate with or without a binder and are exposed to continuous laser beam for desired time in inert gas atmosphere. The process parameters like, laser beam's size and power, speed of scanning, exposure time, compatibility and wettability between coating powders and substrate are some important factors that need to be considered before LSA (Weng *et al.*, 2014). A consolidated study on LSA of aluminum and aluminum alloys are published by Chi *et al.* (2018) and laser cladding on titanium and titanium alloy is published by Weng *et al.* (2014).

Tomida *et al.* (2001) developed 1.5 mm thick TiC/Cu MMC layer on Al-Mg alloy A5083 and realized superior wear resistance LMMCs material with hardness six times as that of Al-Mg alloy.

Co - Extrusion

As defined by Zhao *et al.* (2019) Co-extrusion is a process in which two or more materials are concurrently extruded to form composite. Fig. 9 shows schematic diagram of co-extrusion process. The co-extrusion process is extensively used to develop dissimilar bimetallic composite materials. Researchers also successfully attempted in developing LMMCS using co-extrusion method.

Hassan *et al.* (Hassan and Lewandowski, 2009) developed Al based LMMCs of diameter 15.9 mm where powders of $Al_{89}Ni_3Gd_7Fe_1$ were co-extruded with ~2 mm thick aluminum tube as its surface. The co-extrusion reported was carried out at temperature 673K at extrusion ratio of 20:1. The sample developed shows improved damage tolerance characteristic compared to nano Al composite both in crack arrester and crack divider orientation.

Jamali *et al.* (2010) prepared ingots for co-extrusion by placing DRA (20 vol% SiCp/Al) rods in molten Al. Then the ingots were hot extruded at 400°C and at extrusion ratio 21:1 to form a rectangular bar shaped material. The fabricated material is a unique metal – metal matrix composite where SiCp/Al MMC in the form of continuous rod shape in an aluminum matrix and showed improved fracture toughness compared to SiCp/Al MMC.

Ellis and Lewandowski (1994) developed aluminum based LMMCs Al3003-SiCp/MB-85Al through co-extrusion. Toughness tests on notched and unnotched samples showed no signs of delamination due to strong interfacial bonding achieved during the process.

Spray Atomization and Deposition

Spray atomization and Deposition is a two-stage technique where molten metal in liquid state is disintegrated into micro sized droplets and are deposited to solidify on a substrate. It is also known as spray casting or spray forming (Gupta and Sharon, 2010). Fig. 10 shows the schematic diagram of spray atomization and decomposition process. Single fluid atomization and two-fluid atomization are the two ways of atomizing the molten metal (Apelian *et al.*, 2017). One of the characteristics of the LMMCs processed by spray atomization & deposition is that, no distinct separation between the two layers of metal and MMCs can be observed.

In single fluid atomization, the molten metal is forced through orifice and nozzle to form the atomization of molten metals. In the surface of the molten metal ligament from the orifice, competition between the cohesion force and perturbation force results in the wavy flow stream and with the amplified perturbation force, the liquid jet breaks to form droplets (Bogno *et al.*, 2017). The head of the molten metal before orifice and the external force plays a major role in controlling the atomization. There are various forms of single fluid atomization techniques like drop-on-demand, the pulsated orifice ejection method (POEM), the jet-splitting method, the flat-fan and pressure swirl methods, the centrifugal atomization, the ultrasonic atomization and the Impulse Atomization (IA) technique (Bogno *et al.*, 2017).

In two-fluid atomization, the jet of molten metal interacts with jet of secondary fluid to atomize the molten metal (Anderson and Achelis, 2017). The mechanism of two-fluid atomization is a complex physical phenomenon involving heat and momentum

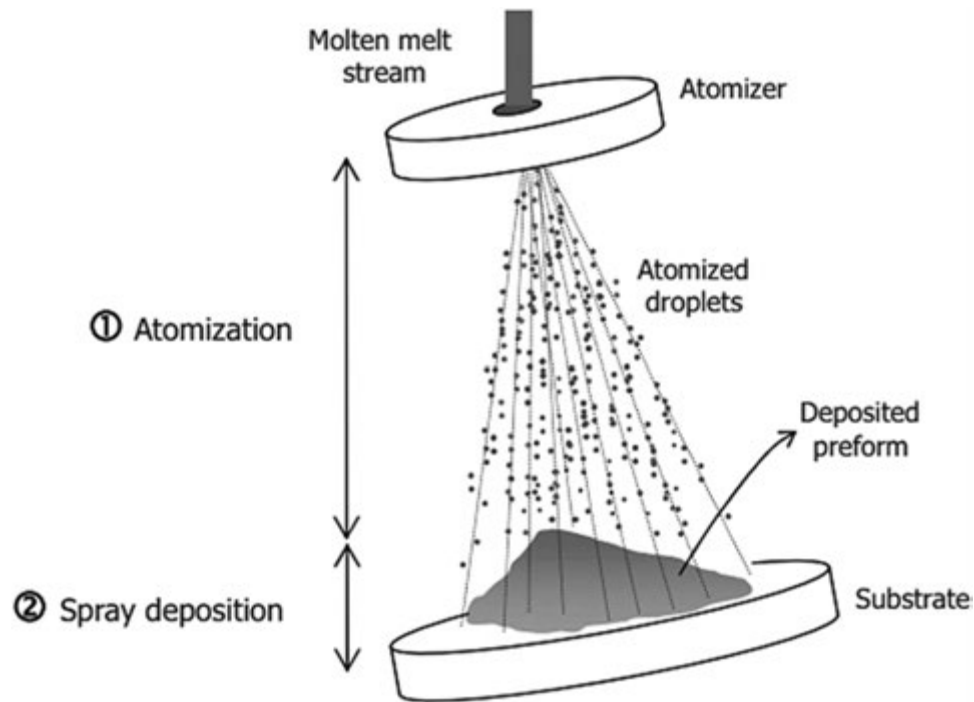


Fig. 10 Schematic diagram representing spray atomization and deposition. Reproduced from Gupta, M., Sharon, N.M.L., 2010. Chapter – 2 Synthesis techniques for magnesium-based materials. Magnesium, Magnesium Alloys, and Magnesium Composites. John Wiley & Sons, Ltd. pp. 13–38.

transfer between the molten metal and secondary fluid (Anderson and Achelis, 2017). Free-Fall Gas Atomization (FFGA), Close-Coupled Gas Atomization (CCGA), Pressure-Swirl Film Formation Plus Gas Jet Disintegration are few other forms of the two-fluid atomization techniques (Anderson and Achelis, 2017).

Xu *et al.* (1998) fabricated layered $\text{SiC}_p/\text{6061}$ MMC using spray atomization and co-deposition. The process involved atomization of Al alloy 6061 by superheating and disintegrating into micro sized droplets using nitrogen gas as secondary fluid followed by injecting SiC_p reinforcements into the spray. Subsequently the atomized alloy and reinforcement particles are co-deposited into water cooled copper substrate. The alternative layers of Al 6061 and $\text{SiC}_p/\text{Al6061}$ were formed by varying particle/reinforcement injecting time, interval and flow rate. The developed LMMCs were subjected to secondary processing of hot isostatic pressing at 540 °C and pressure of 190 MPa for an hour before they were heat treated. No sharp interface or distinct layers of metal and MMC was observed making it significantly different LMMCs. Table 2 lists various mechanical properties, thickness ratio and process utilized in develop LMMCs.

Mechanical Behavior of LMMCs

LMMCs are formed by combination of two materials, with no reaction or limited reaction at their interfaces. The elastic properties and mechanical strengths of the LMMCs can be estimated with the help of rule of mixtures (ROM) and simple bending theory. However, researchers found that, the ductility and toughness do not follow ROM (Syn *et al.*, 1996; Gao *et al.*, 2020; Liu *et al.*, 2014b).

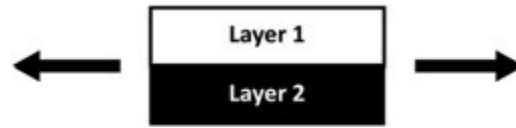
Mechanical Strength of LMMCs

Applicability of the rule of mixtures in estimating strength properties like the yield strength and ultimate strength of LMMCs stands with the assumption that perfect bond exists between the two layers and no slippage occurs between the layers (Shenoi, 1993). It is important to note that the LMMCs exhibit directional properties. Estimation of strength properties using rule of mixtures along longitudinal and transverse direction is described in subsequent sections.

Syn *et al.* (1996) developed dissimilar LMMCs where Mg alloy is coupled with Al based MMC and observed that, ROM holds good even for the laminates without any interdiffusion with maximum deviation in estimated strength value by about 10%. However, ductility estimation based on ROM was not in agreement with experimental value. He reported that the ductility of LMMCs is the function of ductility of interlayer region, delamination, layer thickness, hardness of individual layer and resistance for crack initiation of materials.

Table 2 List of properties of LMMCs along with thickness ratio and manufacturing process

Material	TR ^a	Process	TYS (MPa)	UTS (MPa)	Elongation (%)	References
Ti-3 vol% SiC _p /Al	1.1:1	Hot pressing & rolling	–	341 ± 22	31.4 ± 2.1	Fan <i>et al.</i> (2017)
Ti-5 vol% SiC _p /Al	1.1:1	Hot pressing & rolling	–	351 ± 23	30.6 ± 1.8	Fan <i>et al.</i> (2017)
Ti-10 vol% SiC _p /Al	1.1:1	Hot pressing & Rolling	–	363 ± 25	24.5 ± 1.5	Fan <i>et al.</i> (2017)
Ti-5 vol% (TiB + La ₂ O ₃)/Ti	1:1	Powder Metallurgy & Rolling	–	735	13	Duan <i>et al.</i> (2016)
Ti-10 vol% (TiB + La ₂ O ₃)/Ti	1:1	Powder Metallurgy & Rolling	–	715	17	Duan <i>et al.</i> (2016)
6063Al-(TiB ₂ + TiC) _p /Al	1:1	ARB	–	255.8	11.6	Chen <i>et al.</i> (2020)
Ti-5 vol% TiB _w /Ti	1:1	Diffusion welding	541 ± 6	630 ± 8	19 ± 0.3	Liu <i>et al.</i> (2014a)
Ti-5 vol% TiB _w /Ti	2:1	Diffusion welding	504 ± 5	599 ± 6	27.5 ± 0.2	Liu <i>et al.</i> (2014a)
Ti-5 vol% TiB _w /Ti	1:1	Reaction hot pressing	496	617	20.5	Liu <i>et al.</i> (2013)
8 vol% TiB _w /Ti	–	Diffusion welding	672 ± 6	832 ± 7	5.9 ± 0.2	Liu <i>et al.</i> (2014b)
Ti-8 vol% TiB _w /Ti	1.25:1	Diffusion welding	538 ± 6	673 ± 8	18 ± 0.2	Liu <i>et al.</i> (2014b)
Ti-8 vol% TiB _w /Ti	1:1	Diffusion welding	552 ± 7	689 ± 7	14.1 ± 0.3	Liu <i>et al.</i> (2014b)
Ti-8 vol% TiB _w /Ti	0.75:1	Diffusion welding	569 ± 7	714 ± 6	12.7 ± 0.3	Liu <i>et al.</i> (2014b)
Ti-8 vol% TiB _w /Ti	0.5:1	Diffusion welding	599 ± 8	752 ± 6	9.2 ± 0.4	Liu <i>et al.</i> (2014b)
Ti-8 vol% TiB _w /Ti	0.25:1	Diffusion welding	637 ± 6	789 ± 8	7.9 ± 0.3	Liu <i>et al.</i> (2014b)
Al-5 vol% TiB _w /Ti	1:1	Hot pressing	722	783	8.22	Wu <i>et al.</i> (2016)
Al6061-3.8 vol% SiC _p /Al6061 ^b	–	Spray atomization & Co-deposition	227.5	324.7	16	Xu <i>et al.</i> (1998)
Al6061-4 vol% SiC _p /Al6061 ^b	–	Spray atomization & Co-deposition	232.4	300	6.6	Xu <i>et al.</i> (1998)
Al6061-4.3 vol% SiC _p /Al6061 ^b	–	Spray atomization & Co-deposition	219.3	286.1	7.4	Xu <i>et al.</i> (1998)

^aThickness ratio (thickness of metal layer to thickness of MMC).^boverall volume fraction.**Fig. 11** Laminates under longitudinal loading.

Loading in longitudinal direction

Consider a simple form of laminate with two layers stacked and bonded at its interface. When the bi-layer laminate is subjected to longitudinal axial loading i.e. loading axis is parallel to interface as shown in Fig. 11 and assuming perfect bonding between two layers, laminates exhibit iso-strain behavior upon loading. Iso-strain behavior is the state where each layer has equal strain as that of composites and loads are shared between the layers (Shenoi, 1993). Eqs. (2) and (3) represent the iso-strain condition of LMMCs.

$$\varepsilon_L = \varepsilon_{MMC} = \varepsilon_M \quad (2)$$

$$P_L = P_{MMC} + P_M \quad (3)$$

Where ε and P is strain and load, subscripts L, MMC and M represent laminates, metal matrix composite and metal/alloy respectively. Based on the Eqs. (2) and (3), the strength of the laminate composite can be derived and is called rule of mixture formulation (Shenoi, 1993). The strength of the laminate material based on ROM in terms of volume fraction is given in Eq. (4) (Wu *et al.*, 2016)

$$\sigma_L = v_{MMC} \sigma_{MMC} + v_M \sigma_M \quad (4)$$

Where $\sigma_L, \sigma_{MMC}, \sigma_M$ is strength of the laminate, MMC and monolithic metal/alloy, respectively and v_{MMC}, v_M is the volume fraction of MMC and monolithic metal/alloy, respectively. Liu *et al.* (2014b, 2013) used a generic form of rule of mixture equation to estimate LMMCs properties in terms of thickness.

$$\xi_L = \frac{\xi_{MMC} h_{MMC} + \xi_M h_M}{h_{MMC} + h_M} \quad (5)$$

Where ξ_L, ξ_{MMC} , and ξ_M are the properties like yield strength, ultimate strength and elastic modulus of laminate, MMC and metal/alloy respectively. h_{MMC}, h_M is the thickness of MMC and Metal/alloy layer respectively.

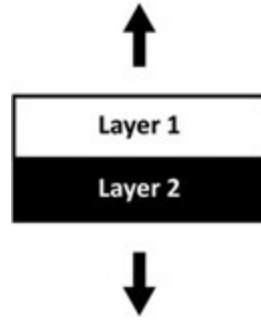


Fig. 12 Laminates under transvers loading.

Loading in transverse direction

Consider a bi-layer laminate subjected to transverse loading i.e. loading axis is perpendicular to the interface, as shown **Fig. 12**. As the cross-sectional area of the laminas are same and assuming perfect bonding at the interface, the laminate exhibit iso-stress behavior. Iso-stress is the state where laminas are subject to same stress. **Eq. (6)** represents the iso-stress condition. From **Eq. (6)**, it can be inferred that in transverse loading condition, the strength of the laminate is equal to the strength of the weakest lamina.

$$\sigma_L = \sigma_{MMC} = \sigma_M \quad (6)$$

In Titanium based LMMC, **Liu et al. (2014b)** observed that as the thickness of Ti is reduced, the theoretical estimation of strength of the laminate based on rule of mixtures was less than the experimental values. **Wu et al. (2016)** described the strength of the laminate as the linear superposition of traditional strengthening and structural strengthening as mentioned in **Eq. (7)**. Traditional strengthening was ascribed to solution strengthening, dispersion and particle strengthening of materials by the reinforcement particles and intermetallics formed between metal/alloy and MMC layers. The structural strengthening was ascribed to redistribution of stress due to load transferring at the interfaces between two layers and inhibiting strain localization thus enhancing stable deformation and damage tolerance of the material. **Wu et al. (2016)** estimated that, 22% of laminate strength is due to the structural strengthening in the developed Ti(Al)-TiBw/Ti LMMCs. **Wu et al. (2016)** asserted that synchronous deformation is impossible to occur in the laminated structure, although each layer participates in the deformation process.

$$\sigma_{laminates} = \sigma_{traditional} + \sigma_{structural} \quad (7)$$

Elastic modulus of LMMCs

Elastic modulus of the LMMCs can be estimated based on rule of mixtures and also using simple bending theory. Based on rule of mixture, elastic modulus of the laminate in longitudinal direction, assuming perfect bonding between interface and iso-strain condition, is given by (**Shenoi, 1993**):

$$E_L = \nu_{MMC} E_{MMC} + \nu_M E_M \quad (8)$$

Similarly, based on rule of mixture, elastic modulus of laminate in transverse direction, assuming perfect bonding between interface and iso-stress condition, is given by (**Shenoi, 1993**):

$$E_L = \frac{1}{\frac{\nu_{MMC}}{E_{MMC}} + \frac{\nu_M}{E_M}} \quad (9)$$

Where E_L , E_{MMC} and E_M is the elastic modulus of laminate, MMC and metal/alloy, respectively. Apart from rule of mixture, **Smith et al. (1997)** proposed utilizing simple bending theory to predict elastic modulus of LMMCs under bending. **Smith et al. (1997)** found that the estimated effective young's modulus using simple bending theory was in excellent agreement with experimental results from four-point bending test for developed Ti based LMMCs. As proposed by **Smith et al. (1997)** an effective Young's modulus in bending for the LMMCs is given by **Eq. (10)** and **Fig. 13** shows the various parameters used in bending theory analysis.

$$E_b = \frac{3}{2t^3} \frac{M}{R} \quad (10)$$

Where, E_b , $2t$, and $\frac{M}{R}$ are effective young's modulus in bending, thickness of LMMCs and bending stiffness, respectively. The bending stiffness is given by the **Eq. (11)**

$$\frac{M}{R} = \frac{2}{3} \sum_{n=1}^k E_k (z_k^3 - z_{k-1}^3) \quad (11)$$

Here, M is the bending moment per unit width b and R is the inverse curvature of the neutral axis of the beam bending stiffness, respectively. It can be noticed that the estimation of young's modulus using rule of mixture is insensitive to the stacking sequence where as simple bending theory is sensitive to stacking sequence. **Smith et al. (1997)** developed "C" and "S" types of tri-layer

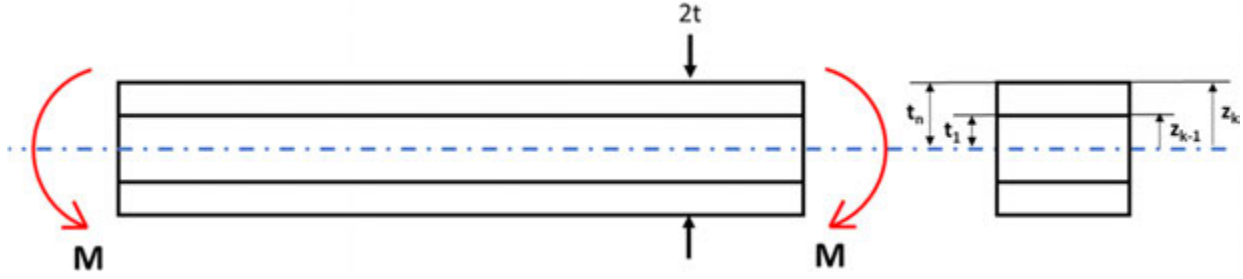


Fig. 13 Schematic diagram showing various parameters of LMMCs used in bending theory analysis. Redrawn from Smith, D.J., Zuo, Y.Q., Partridge, P.G., Wisbey, A., 1997. Bend stiffness and strength of laminates composed of titanium alloy and titanium metal matrix composite. *Materials Science and Technology* 13 (1), 35–40. doi:10.1179/mst.1997.13.1.35.

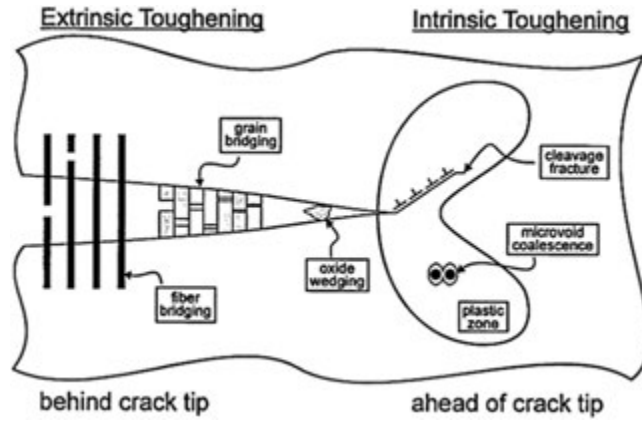


Fig. 14 Diagram showing extrinsic and intrinsic toughening in materials. Reproduced from Launey, M.E., Ritchie, R.O., 2009. On the fracture toughness of advanced materials. *Advanced Materials* 21 (20), 2103–2110. doi:10.1002/adma.200803322.

LMMC, where C type laminate had MMCs as mid layer and S type had monolithic Ti Alloy as mid layer. The young's modulus estimated based on simple bending theory in S type LMMC was higher than C type LMMC.

Density of LMMCs

Density of the LMMCs can also be estimated based on the rule of mixture. The density (ρ) of the LMMCs in terms of volume fraction and thickness (Liu *et al.*, 2014b, 2013) of lamina is given Eqs. (12) and (13) respectively.

$$\rho_L = v_{MMC} \rho_{MMC} + v_M \rho_M \quad (12)$$

$$\rho_L = \frac{\rho_{MMC} h_{MMC} + \rho_M h_M}{h_{MMC} + h_M} \quad (13)$$

Fracture Mechanics of LMMCs

LMMCs outshine MMCs in ductility, resistance for crack initiation and crack propagation. There are numerous researches attempting to understand the fracture mechanics of LMMCs. This section of the article makes an attempt to summarize results of various researches to understand the phenomena of damage tolerance and enhanced toughness of LMMCs.

The increase in the toughness of the LMMCs can be attributed to intrinsic and extrinsic toughening mechanism (Liu *et al.*, 2014b; Sills and Thouless, 2015). Intrinsic toughening mechanisms occur ahead of the crack tip (Sills and Thouless, 2015). Intrinsic toughening is generally governed by the intrinsic properties like precipitates, particle spacing, grain size, particle size, particle distribution, reinforcement type, quantity of reinforcement, matrix condition, morphology etc (Liu *et al.*, 2014b; Osman *et al.*, 2008). The Intrinsic properties are related to individual material layers of LMMCs. Modification in these intrinsic properties can improve the fracture resistance of metals and MMCs (Osman *et al.*, 2008). Extrinsic toughening mechanism occurs behind the crack tip. Few phenomena of extrinsic toughening are crack bridging, stress transferring or unloading at crack wake (Sills and

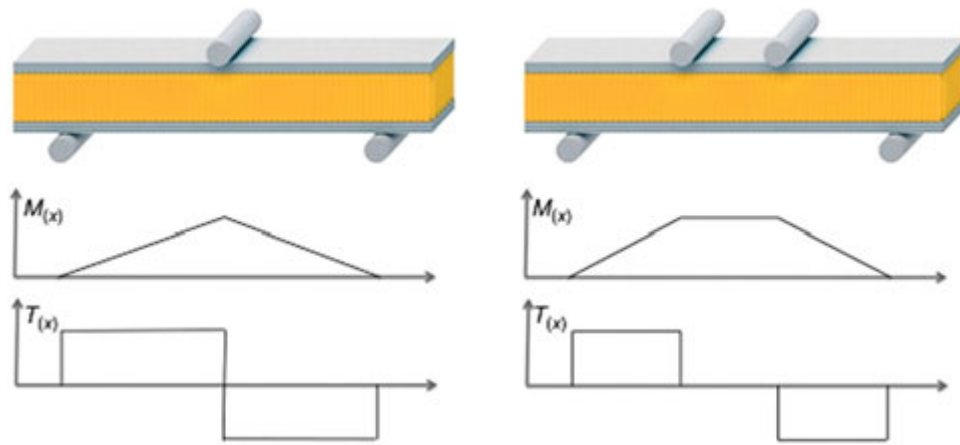


Fig. 15 Schematic diagram of three-point bending and four-point bending test and their corresponding bending moment diagram and transverse force diagram. Reproduced from Volker Altstädt, A.F., 2015. Chapter 8 – Mechanical properties of multifunctional foam core materials. In: Friedrich, K., Breuer, U. (Eds.), *Multifunctionality of Polymer Composites*. Oxford: William Andrew Publishing, pp. 262–301.

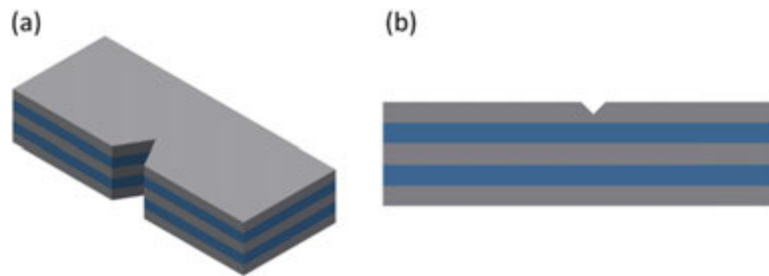


Fig. 16 Schematic diagram showing: (a) Crack divider (b) Crack arrester configuration notched samples.

Thouless, 2015) leading to interfacial delamination and crack deflection (Liu *et al.*, 2014b). Fig. 14 shows intrinsic and extrinsic toughening mechanisms in material.

Generally, notched specimen is used to measure toughness of LMMCs. Three-point bending test, four-point bending test, compact testing, Charpy V-notch impact test are few tests employed by various researchers to understand the bending, fracture and impact behavior of LMMCs. One of the major differences between three-point bending and four-point bending test is in the nature of loading the specimen. In 4 point, the center portion of the specimen is subjected only to uniform bending moment. Fig. 15 shows the schematic diagram of three-point and four-point bending test.

Depending on the notch orientation or loading orientation, crack divider and crack arrester are the two configurations of test samples predominantly used to measure toughness of the LMMCs. In crack divider configuration, the loading direction is parallel to layers/interface and the notch in the sample is shared with all the layers as shown in Fig. 16(a). In crack arrester configuration, the loading direction is perpendicular to the layers/interface and the notch in the sample lies either in metal or MMC layer as shown in Fig. 16(b). Depending on the notch orientation or loading, the samples show different fracture mechanism (Osman *et al.*, 2008).

Fracture of samples with notch/loading in crack divider orientation

Osman *et al.* (1994) carried out a tensile test in a crack divider notched specimen of Al based laminate 7093–15 vol% SiC_p/7093. He observed non catastrophic failure in LMMCs against a catastrophic failure of MMC 15 vol% SiC_p/7093. They (Osman *et al.*, 1994) described the failure of the LMMCs as step wise process: (1) initiation, (2) arrest, (3) re-initiation and (4) subsequent arrest. He explained that the stable crack growth of LMMCs was due to the energy absorbed by the ductile Al7093 material at crack wake reducing energy for crack propagation. Osman *et al.* (1994) stated that the crack stability depends on the new surface formation energy and the material energy absorption. The ductile layer in the LMMCs effectively reduces the stress intensity levels at crack tip promoting stable crack growth. When the ductile layer fails, all the load concentrate near the crack tip and hence, the unstable crack growth.

Further Osman (Osman *et al.*, 2008) performed three-point bending test on crack divider notched specimen of Al based laminate 7093–15 vol% SiC_p/7093. He observed an improved toughness of the LMMCs than MMC. Apart from stable crack growth, the post-mortem analysis revealed that the extent of crack growth in MMCs was larger than Al alloy. Like in (Osman *et al.*, 1994), the stable crack growth was due to the crack bridging phenomena by the irreversible plastic deformation of ductile ligament

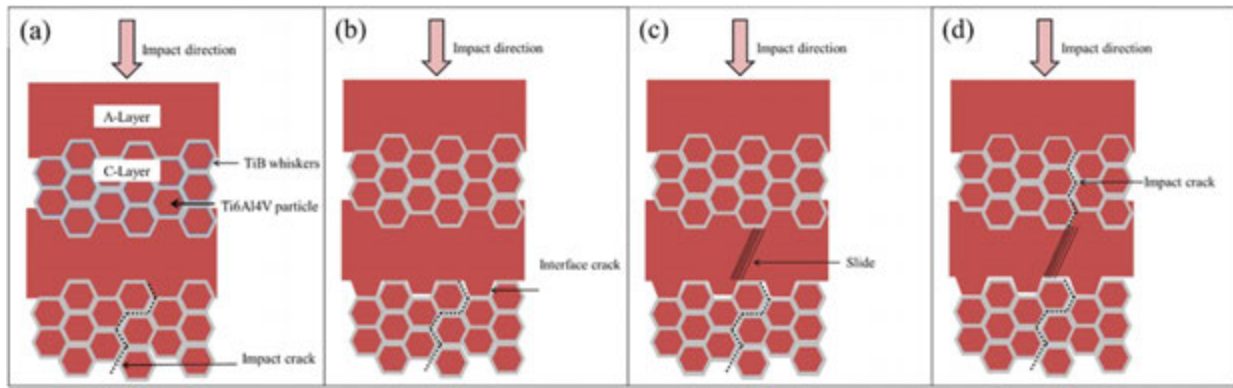


Fig. 17 Diagram representing Wang *et al.* explanation of fracture in LMMC. Reproduced from Wang, S., Huang, L., An, Q., Geng, L., Liu, B., 2018. Dramatically enhanced impact toughness of two-scale laminate-network structured composites. *Materials & Design* 140, 163–171. doi:10.1016/j.matdes.2017.11.067.

at the crack wake of MMCs absorbing the energy. Thus, confirming the crack bridging as the dominate mechanism in enhancing toughness of the LMMCs in crack divider configuration test specimen. Osman (Osman *et al.*, 2008) also pointed that, the delamination also improved the toughness of the LMMCs. He theorized that in crack bridging, the effectiveness of the ligament is directly proportional to the toughness of the bridge material.

Hassan *et al.* (Hassan and Lewandowski, 2009) developed nanoscale aluminum metal matrix composite sandwiched with pure Al by co-extrusion process and studied the bending ductility and fracture toughness. The nanoscale Al MMCs exhibited catastrophic failure in 3-point bending test and its LMMCs with Al had non catastrophic failure. When the test was performed in crack divider-oriented notch specimen, load drop in the load -displacement curve was observed. Later there was increase in the load carrying capacity of the material before final failure. Similar observation was also made in tri-layer LMMCs. The observation by Hassan also shows step wise fracture behavior as explained by Osman (Osman *et al.*, 1994).

Miracle *et al.* (2001) developed Al based LMMCs Al3003–15 vol% SiC_p/7093 with varying heat treatment and carried out fracture toughness test in a crack divider notched test sample. The LMMCs had 79% and 53% improvement in toughness compared to DRA (MMC) in underaged and peak-aged condition samples, respectively.

Fracture of samples with notch loading in crack arrester orientation

Wang *et al.* (2018) studied the bending and impact toughness of titanium based LMMCs in an unnotched and notched sample along crack arrester loading orientation. He also noted that, the developed LMMCs had superior toughness than its MMC counterpart. During the impact loading, the MMC took more loading than monolithic metal, resulting in breakage of whisker shaped reinforcements due to poor stress transferring reinforcement and unstable crack propagated along boundaries where local volume fraction of reinforcement was high. But in LMMCs, there is an alternative layer of metal which in general has higher toughness, is stacked between MMCs. As crack reaches the interface, metal layer offers a resistance and stops the crack propagation as metals slips and orients favoring whisker reinforcements to transfer loads effectively. Further, the impact load generates crack in the metal layer near interface which propagates in a stable fashion. Fig. 17 pictorially explains the fracture mechanics of LMMC as described by Wang *et al.* (2018). The metal layer in the LMMCs creates crack deflection and blunting resulting in enhanced toughness and ductility. However, the failure mechanism of LMMCs in crack arrester orientation is different from crack divider orientation. Impact test results of Ti-TiBw/Ti LMMCs by Wang *et al.* (2018) showed stage wise failure behavior as described by Osman *et al.* (1994).

Osman *et al.* (2008) also performed three-point bending test of Al based LMMCs with notch along crack arrester orientation. When the test samples are subjected to three-point bending test, the delamination between the notch layer and the adjacent DRA layer occurs before the crack propagates to DRA MMCs. Due to this, the triaxial stress is reduced ahead of crack tip. Once the crack reaches the delaminated region, the sample, now, behaves like an unnotched sample. The crack then initiates in the DRA MMCs and propagates rapidly. Before the crack reaches the ductile layer the delamination between the layer occurs and finally the energy absorption is associated with the monolithic material. Fig. 18 schematically represents the fracture mechanism as explained by Osman *et al.* (2008). Among the samples developed through roll bonding with foil, roll bonding and adhesive bonding, the roll bonded samples with foil exhibited highest fracture toughness and adhesive bonded laminate had least fracture toughness and was attributed to the greater degree of delamination in the roll bonded samples with foil and least by adhesive layer.

Hassan *et al.* (Hassan and Lewandowski, 2009) performed three-point bending test in crack arrester oriented notched sample of Al based LMMC. The test results showed drop in the load after some initial loading in load displacement graph, suggesting the crack initiation and rapid growth, however the sample had higher fracture toughness than MMCs due to Al layer. The fracture behavior of the sample developed by Hassan *et al.* (Hassan and Lewandowski, 2009) was similar as that of Osman *et al.* (2008). The load – deflection curve for crack arrester notched samples of Ti based LMMC samples developed by Liu *et al.* (2016) also exhibited similar results as of Osman *et al.* (2008). Liu *et al.* (2016) described it as “pop-in” fracture behavior. As the samples

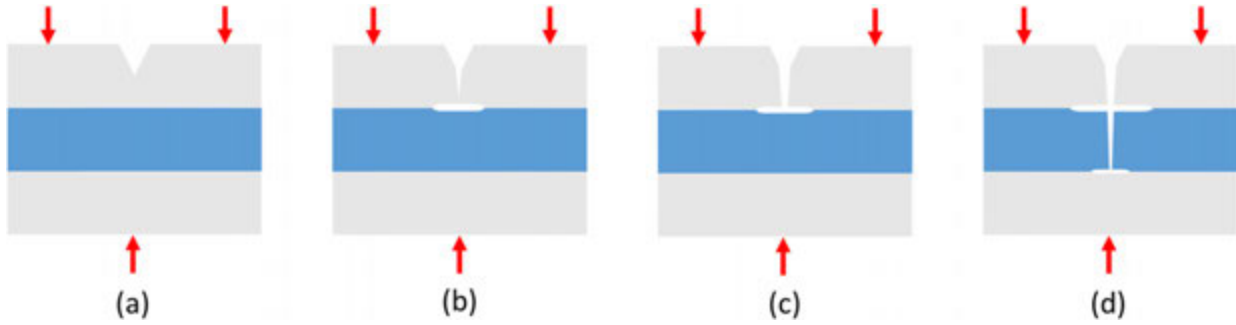


Fig. 18 Schematic diagram representing fracture mechanism of crack arrester oriented notched sample in three-point bending test. Redrawn from Osman, T.M., Hassan, H.A., Lewandowski, J.J., 2008. Interface effects on the quasi-static and impact toughness of discontinuously reinforced aluminum laminates. *Metallurgical and Materials Transactions A* 39 (8), 1993–2006. doi:10.1007/s11661-008-9538-x.

developed were multilayered, the cycle of crack initiation, arrest, re-initiation and subsequent arrest continued until the final layer. Delamination, crack deflection and blunting mechanism were dominant mechanisms in improving the toughness of the LMMCs. In LMMCs, if the material satisfies the equation proposed by Osman *et al.* (2008) then crack at the interface gets deflected instead of progressing through the next layer.

$$\frac{G_{ic}}{G_{fc}} \leq \frac{h_m E_m + h_f E_f}{h_f E_f} \left(\frac{1}{4\pi(1 - \nu^2)} \right) \quad (14)$$

Here, G_{ic} and G_{fc} are the fracture energies of the interface and uncracked layer, respectively; h_m and h_f are the thickness of the cracked matrix and uncracked layer, respectively; E_m and E_f are the Young's moduli of the cracked matrix and uncracked layer, respectively and ν is Poisson's ratio.

Delamination

Delamination in the LMMCs is due to weaker interfacial bonding. Sample which exhibits minimal delamination is due to stronger interfacial bond between the layers. Stronger interfacial bonding in LMMCs offers less resistance for crack propagation at interface. Hence cracks propagate to adjacent layers with ease and cracks propagation is prevented as long as the monolithic metal/alloy layers resist it. Osman *et al.* (2008) utilizes Eq. (14) to understand the energy absorption due to delamination in LMMCs.

$$W_d = 2f\sigma_0nd \quad (14)$$

Where W_d is the energy absorbed during delamination, f , σ_0 and n is the volume fraction, flow stress and work hardening coefficient of ductile material, respectively and d is the delamination length.

Zhang and Lewandowski (1997) studied delamination in samples with crack arrester notched samples using four point bending test. They found that, the samples with higher delamination i.e., weaker interfacial strength, had higher toughness than samples with lesser delamination. However, Zhang and Lewandowski (1997) and Miracle *et al.* (2001) pointed that, the weaker interfacial strength results in weaker tensile strength highlighting the importance of interfacial strength on structural integrity. If K_I is the stress intensity factor of laminate with notch to interface distance d , then the strength of the interface is given by (Zhang and Lewandowski, 1997):

$$\sigma_f = \frac{K_I}{(2\pi d)^{0.5}} \quad (15)$$

Similar observation was made by Liu *et al.* (2016) in titanium based LMMCs Ti-TiB_w/Ti, where the crack arrester notched samples with weaker interfacial bonding had larger extent of delamination and superior fracture toughness. Wang *et al.* (2019) used ABAQUS simulation to estimate the interfacial strength in Ti based LMMCs. The interfacial bonding strength was estimated as the difference between the maximum stress estimated in the adjacent layers.

$$\sigma_{\text{interface stress difference}} = \sigma_{\text{outermost-layer-max}} - \sigma_{\text{adjacent-layer-max}} \quad (16)$$

Hence, the energy absorbed by the samples depends on the interfacial bonding properties. Osman *et al.* (2008) observed that, delamination did not change the peak loading, but had drastic improvement in the total deflection. Hence, it can be inferred that the delamination is an important phenomenon aiding toughness enhancement in LMMCs. The energy consumed by the delamination will reduce the energy available for propagation in both MMCS and Al alloy layers (Osman *et al.*, 2008). Delamination is favorable when materials are subjected to impact loading or a severe loading condition (Miracle *et al.*, 2001). The interfacial bonding on the layers are one of the vital parameters of LMMCs to achieve ductility, toughness, tensile properties and structural integrity. In a given laminate the interfacial bonding is majorly controlled by the manufacturing process.

Hosseini Monazzah *et al.* (2014) utilized shear test to determine the interfacial strength of the laminates. He developed Al based MMC Al1050-SiC_p/Al6061 via roll bonding process with varying rolling strain and volume % of SiC_p reinforcements. He found that the interfacial strength increased with increase in number of rolling pass and it decreased with increase in amount of

SiC_p reinforcement. During rolling process, due to multiple pass of rolling, the laminates will be subjected to increased rolling strain, higher pressure and also longer diffusion time (Hosseini Monazzah *et al.*, 2014). The increased rolling strain results in larger surface area contact between metal and MMC layers. This creates stronger bonding between the layers resulting in higher shear strength of the laminates. In the roll bonding process, the interfacial adhesion can be controlled by the rolling strain, as increase in rolling strain increases the interfacial adhesion (Hosseini Monazzah *et al.*, 2014; Monazzah *et al.*, 2013). Monazzah *et al.* (2013) also found that, plastic deformation and delamination are the major source of energy absorption that leads to increase in toughness and damage tolerance. Monazzah *et al.* (2013) also found that the delamination energy absorption decreased with increase in roll strain. Increase in roll strain increased the interfacial bonding, hence supporting Osman *et al.* (2008) findings: delamination energy absorbed is directly proportional to delamination length in LMMCs.

Wang *et al.* (2019) developed Ti based LMMCs with very high interfacial strength of 777 ± 52 MPa which is 90% of matrix strength via powder metallurgy technique.

Design Considerations of LMMCs

There are various parameters which influence the overall properties of LMMCs. Broadly, parameters like stacking sequence, stacking layer thickness, stacking layer materials and manufacturing processes are vital in designing the intended LMMCs. A thorough understanding on effects of various parameters on mechanical properties of the LMMCs assists while designing or deciding on LMMCs for a desired application. Subsequent section of this article makes an attempt to summarize the effects of various parameters on the LMMCs properties.

Stacking sequence

LMMCs with different stacking arrangements exhibit different material properties. Stacking sequence plays a key role in enhancing the damage tolerance and toughness of the laminated material by manipulating the crack propagation and blunting of the crack. Although there are a number of stacking arrangements possible considering various directional properties of metal and MMCs, the bi-material LMMCs fundamentally have four stacking arrangements. In case of multilayer LMMCs stacking arrangements are the combination of multiple bi-layer or tri-layer stacking sequences. Fig. 19 shows the hierarchy of stacking sequence and Fig. 20 shows the four fundamental stacking sequences.

Partridge *et al.* (1996) studied C-M-C and M-C-M configurations in Ti Based LMMC. Using the Ti alloy property, the C-M-C and M-C-M configured laminated were normalized to assign property ranking ratio. Based on the Ranking method, C-M-C configuration showed superior overall impact properties (Partridge *et al.*, 1996). Smith *et al.* (1997) proposed using simple bending theory to estimate the bending elastic modulus of the laminate which is sensitive to stacking sequence. As per proposed estimation method by Smith *et al.* (Kazakov, 1985b), farther the lamina with higher elastic modulus from the center of the laminate, higher the elastic modulus of laminate structure.

Wang *et al.* (2019) used simulation technique using ABAQUS tool and Johnson-cook material model to understand the effect of the stacking sequence of quad-layer titanium based LMMCs on bending behavior. The two quad-layer LMMCs are of sequence M-C-M-C and C-M-C-M which is basically formed by stacking two M-C and C-M stacking sequence, respectively. From the simulation and experimental results, the LMMCs with C-M stacking sequence had superior overall mechanical properties with double the bending strain and triple the toughness as compared to M-C configuration. The superior fracture toughness and

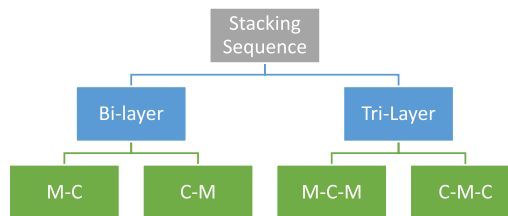


Fig. 19 Chart showing four stacking configurations.



Fig. 20 Schematic diagram of fundamental stacking configurations of LMMCs.

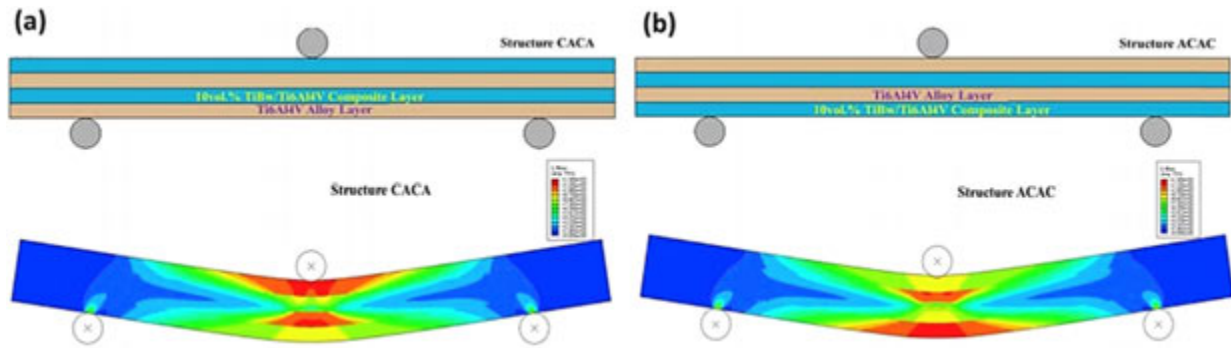


Fig. 21 Simulation results of three-point bending test from Wang *et al.* showing the stress in laminas of LMMCs (a) C-M-C-M configuration (b) M-C-M-C configuration. Reproduced from Wang, S., *et al.*, 2019. Regulating crack propagation in laminated metal matrix composites through architectural control. *Composites Part B: Engineering* 178, 107503. doi:10.1016/j.compositesb.2019.107503.

bending strain of C-M configuration is attributed to the crack blunting by the alloy layer (Wang *et al.*, 2019). Fig. 21 shows stacking arrangements and stress contouring of LMMCs in three-point bending test from Wang *et al.* (2019).

Stacking Layer Thickness

LMMCs are formed by stacking alternative layers of metal and MMCs basically to achieve higher toughness. The metal/alloy layer introduced in LMMCs improves the toughness majorly by crack bridging, crack blunting and deflecting. The toughness of the material depends on the thickness of the material as long as thickness is below the limit as mentioned in the Eq. (17) and toughness of the material is insensitive to thickness if the sample thickness is greater than that suggested by Eq. (17). As the thickness reduces below the value estimated from the Eq. (17), the toughness of the material K_{IQ} increases. Hence, the least toughness of the material is exhibited at plane strain condition when the thickness of the samples satisfies the Eq. (17) (Dowling, 2013).

$$t \geq 2.5 \left(\frac{K_Q}{\sigma_0} \right)^2 \quad (17)$$

The metal and MMC lamina in LMMCs can have similar or dissimilar thickness. Based on the thickness ratio (TR) i.e., thickness of metal/alloy layer to thickness of MMC, three configurations of LMMCs can exist $TR > 1$, $TR = 1$ and $TR < 1$. Liu *et al.* (2016) and Wang *et al.* (2019) reported that, if the thickness of the composite material layer satisfies the Eq. (18), the tunneling crack propagation can be suppressed.

$$t_{\text{composite layer}} \leq \frac{2\sqrt{3}K_{IC(\text{composite layer})}^2 \sigma_{s(\text{alloy layer})}}{\sigma_{\text{composite layer}}^3} \quad (18)$$

Where, $t_{\text{composite layer}}$ is the composite layer thickness, $K_{IC(\text{composite layer})}$ is the fracture toughness of the composite layer, $\sigma_{s(\text{alloy layer})}$ is the yield stress of the alloy layer and $\sigma_{(\text{composite layer})}$ stress in the composite layer.

Liu *et al.* (2014b) studied the effect of Ti layer thickness in Ti based LMMC Ti-TiBw/Ti. He developed LMMCs with TR ranging from 0.25 to 1.25. He found that with decrease in the thickness ratio, the strength of the Ti-TiBw/Ti laminate increased and ductility decreased with severe necking. Due to lack of plastic deformation zone, the fracture behavior of the laminate had ductile to brittle transition (DBT). With Increase in TR he found an effective blunting of crack tips resulting in increased resistance for crack propagation. Syn *et al.* (1996) reported that, reducing the thickness of individual layer enhances the ductility of LMMCs which is attributed to difficulty in delamination in developed Mg – Al MMC laminate.

Ellis and Lewandowski (1994) studied the effect of layer thickness on the impact toughness of DRA laminated materials. They used crack arrester notched sample with ductile layer thickness of 0.8–2 mm below the notch. They found that the LMMC absorbed energy more than the MMC regardless of the ductile layer thickness and the increase in toughness with increase in ductile layer thickness from 0.8 to 2 mm below the notch was 1/3rd of initial increment. The improvement in the toughness was attributed to the decrease in global volume percentage of reinforcement and effective crack shielding and deflection by the ductile layer.

Hassan *et al.* (2004b) studied the fatigue crack propagation in Aluminum based LMMCs Al6013–25 vol% SiCp/Al6090 (diffusion bonding) under fatigue load ratios of 0.1 and 0.3. Developed samples were thick and thin LMMCs with crack arrester notched specimens. The metal/MMC layer thickness in thick and thin LMMCs were 0.8 mm/0.64 mm ($TR = 1.25$) and 0.36 mm/0.36 mm ($TR = 1$) respectively. The LMMCs with thicker layer samples had better fatigue performance compared to thinner specimens. Along with improved fracture toughness, the LMMCs had increased fatigue threshold, and decreased Paris-law slopes showing improved fracture crack growth resistance. Hoffman and Gibeling (1995) developed Al based LMMCs Al5182–25 vol% SiCp/Al6090 through diffusion bonding. From the results Hoffman and Gibeling (1995) concluded that LMMCs had higher fatigue crack growth resistance but had lower fatigue threshold.

Stacking Layer Materials

From the earlier discussions, it is known that individual material properties define the overall property of the LMMCs. Especially, selection of ductile materials in LMMCs depends on the required lower yield strength, ductility, thickness and material availability (Miracle *et al.*, 2001). In case of dissimilar metal LMMCs, the possibility of formation of intermetallics near the interface must be accounted during the selection or design stage (Tomida *et al.*, 2001; Syn *et al.*, 1996; Wu *et al.*, 2016).

Generally, MMCs are designated based on volume percentage of reinforcement and matrix. In the LMMCs, with the introduction of the metal/alloy layers, volume fraction of reinforcement is obviously lesser than the volume fraction of reinforcement in MMC lamina. The volume fraction of reinforcement in LMMCs are also called as global volume percentage of reinforcement. Wang *et al.* (2018) found that, increase in the amount of the reinforcement increased the resistance for crack propagation and decreased the energy absorption during plastic stage. On the other hand, Duan *et al.* (2016) found that increase in the volume percentage of reinforcement from 5% to 10% increased the mechanical properties of Ti - (TiB + La₂O₃)/Ti but further increase of volume fraction of reinforcements from 10% to 15% reduced the ductility of the LMMCs.

Xu *et al.* (1998) developed a unique LMMCs where he introduced reinforcement particles in the matrix of Al alloy at different layers forming Alloy – MMC laminate. His observation was that the material portion or layers with higher volume percent of reinforcement was the site of crack initiation. Similarly, Wang *et al.* (2019) observed higher ratio of K_I/K_{IC} in MMC layers during the simulation studies in Ti based LMMCs and predicted MMC as the site of crack initiation. Fig. 21 shows the simulation results of Ti Based LMMCs (Wang *et al.*, 2019). Ellis and Lewandowski (1994) and Liu *et al.* (2013) agree to the point that the MMCs are the site of crack initiation. Toughness of MMCs can be enhanced based on the reinforcement type, size, volume fraction, and distribution (Wang *et al.*, 2019). However, details on enhancing the fracture toughness of MMC is beyond the scope of this article.

Applications

LMMCs are used in various fields like aerospace, automotive, electronic devices, military applications, etc (Ko and Jackson, 1993; Tomida *et al.*, 2001; Liu *et al.*, 2014b). Superior high temperature mechanical properties, relatively higher toughness than MMCs, higher damage tolerance and ductility are few characteristics of LMMCs. Due to these properties, LMMCs are used in hot structural applications like, hypersonic flight vehicle (Ko and Jackson, 1993).

Salzar (1999) demonstrated the feasibility of using LMMC instead of monolithic material in aircraft engine shaft using simulation technique. Apart from strength based applications, LMMCs are also used in wear based applications (Tomida *et al.*, 2001). In applications demanding high wear resistance and hardness, thin layer of coating is not suitable and thick layer of hard material is required. Tomida *et al.* (2001) developed a thick layer of the MMC on top of soft aluminum substrate using laser surface alloying forming LMMC.

As discussed earlier, LMMCs show directional properties depending on the individual material used in construction. LMMC structures offer lower thermal conductivity along thickness direction, which will be of great advantage in applications like hypersonic flights where combined thermal and mechanical stress are usual (Ko and Jackson, 1993).

LMMCs are advanced metal matrix composites and relatively new class of materials. Lack of data hinders the wide spread use of LMMCs (Salzar, 1999). Apart from improving toughness, damage tolerance and ductility, LMMCs have the potential to reduce the cost of MMCs due to introduction of low cost ductile/soft monolithic metal/alloy layer (Zuo *et al.*, 1998).

References

- Anderson, I.E., Achelis, L., 2017. Two fluid atomization fundamentals. In: Henein, H., Uhlenwinkel, V., Fritsching, U. (Eds.), *Metal Sprays and Spray Deposition*. Cham: Springer International Publishing, pp. 49–88.
- Apelian, D., Henein, H., Fritsching, U., 2017. Introduction. In: Henein, H., Uhlenwinkel, V., Fritsching, U. (Eds.), *Metal Sprays and Spray Deposition*. Cham: Springer International Publishing, pp. 1–7.
- Bogno, A.-A., Henein, H., Uhlenwinkel, V., Gärtner, E., 2017. Single fluid atomization fundamentals. In: Henein, H., Uhlenwinkel, V., Fritsching, U. (Eds.), *Metal Sprays and Spray Deposition*. Cham: Springer International Publishing, pp. 9–48.
- Chaklader, A.C.D., 1965. Reactive hot pressing: A new ceramic process. *Nature* 206 (4982), 392. doi:10.1038/206392a0.
- Chen, Y., *et al.*, 2020. Revealing hetero-deformation induced (HDI) stress strengthening effect in laminated Al-(TiB₂ + TiC)p/6063 composites prepared by accumulative roll bonding. *Journal of Alloys and Compounds* 815, 152285. doi:10.1016/j.jallcom.2019.152285.
- Chi, Y., Gu, G., Yu, H., Chen, C., 2018. Laser surface alloying on aluminum and its alloys: A review. *Optics and Lasers in Engineering* 100, 23–37. doi:10.1016/j.optlaseng.2017.07.006.
- Dowling, N.E., 2013. *Mechanical Behavior of Materials: Engineering Methods for Deformation, Fracture, and Fatigue*, fourth ed. Boston: Pearson.
- Duan, H., Han, Y., Lu, W., *et al.*, 2016. Configuration design and fabrication of laminated titanium matrix composites. *Materials & Design* 99, 219–224. doi:10.1016/j.matdes.2016.03.061.
- Ellis, L. Yost, Lewandowski, J.J., 1994. Effects of layer thickness on impact toughness of Al/AISiCp laminates. *Materials Science and Engineering: A* 183 (1), 59–67. doi:10.1016/0921-5093(94)90890-7.
- Everett, R.K., 1991. 2 - Diffusion bonding. In: Everett, R.K., Arsenault, R.J. (Eds.), *Metal Matrix Composites: Processing and Interfaces*. Academic Press, pp. 17–42.
- Fan, G., *et al.*, 2017. Improving the tensile ductility of metal matrix composites by laminated structure: A coupled X-ray tomography and digital image correlation study. *Scripta Materialia* 135, 63–67. doi:10.1016/j.scriptamat.2017.03.030.
- Forster, J.A., Jha, S., Amatruda, A., 1993. The processing and evaluation of clad metals. *JOM* 45 (6), 35–38. doi:10.1007/BF03223308.

- Gupta, M., Sharon, N.M.L., 2010. Chapter – 2 Synthesis techniques for magnesium-based materials. In *Magnesium, Magnesium Alloys, and Magnesium Composites*. John Wiley & Sons, Ltd. pp. 13–38.
- Gao, K., *et al.*, 2020. The deformation characteristics, fracture behavior and strengthening-toughening mechanisms of laminated metal composites: A review. *Metals* 10 (1), 4. doi:10.3390/met10010004.
- Hassan, H.A., Lewandowski, J.J., 2009. Laminated nanostructure composites with improved bend ductility and toughness. *Scripta Materialia* 61 (11), 1072–1074. doi:10.1016/j.scriptamat.2009.08.034.
- Hassan, H.A., Lewandowski, J.J., Abd El-Latif, M.H., 2004a. Effects of changes in temperature on fatigue crack growth of adhesively bonded Al 2080/SiC/20p-2080 Al laminated composites. *Journal of Materials Science* 39 (9), 3063–3067. doi:10.1023/B:JMSC.0000025833.03662.34.
- Hassan, H.A., Lewandowski, J.J., Abd El-Latif, M.H., 2004b. Effects of lamination and changes in layer thickness on fatigue-crack propagation of lightweight laminated metal composites. *Metallurgical and Materials Transactions A* 35 (1), 45–52. doi:10.1007/s11661-004-0107-7.
- Hoffman, P.B., Gibeling, J.C., 1995. Near-threshold fatigue crack growth in aluminum composite laminates. *Scripta Metallurgica et Materialia* 32 (6), 901–906. doi:10.1016/0956-716X(95)93222-P.
- Hosseini Monazzah, A., Pouraliakbar, H., Bagheri, R., Seyed Reihani, S.M., 2014. Toughness behavior in roll-bonded laminates based on AA6061/SiCp composites. *Materials Science and Engineering: A* 598, 162–173. doi:10.1016/j.msea.2014.01.014.
- Jamali, M., Farokhzadeh, Kh, Bagheri, R., Seyed Reihani, S.M., 2010. Architecturally modified Al–DRA composites: the effect of size and shape of the DRA rods on fracture behavior. *Journal of Materials Science* 45 (11), 2852–2861. doi:10.1007/s10853-010-4273-2.
- Kannan, R., Rangaraj, L., 2018. Densification of ZrCx-ZrB2 composites by reactive hot pressing at low applied pressure. *Metallurgical and Materials Transactions A* 49 (8), 3539–3549. doi:10.1007/s11661-018-4647-7.
- Kaw, A.K., 2006. *Mechanics of Composite Materials*, second ed. Boca Raton, FL: Taylor & Francis.
- Kazakov, N.F., 1985a. Chapter 1 – An outline of diffusion bonding in vacuum. In: Kazakov, N.F. (Ed.), *Diffusion Bonding of Materials*. Pergamon, pp. 10–16.
- Kazakov, N.F., 1985b. Chapter 2 – A theory of diffusion bonding. In: Kazakov, N.F. (Ed.), *Diffusion Bonding of Materials*. Pergamon, pp. 17–48.
- Ko, W.L., Jackson, R.H., 1993. Compressive and shear buckling analysis of metal matrix composite sandwich panels under different thermal environments. *Composite Structures* 25 (1–4), 227–239. doi:10.1016/0263-8223(93)90169-Q.
- Lee, H.-S., 2012. Chapter 10 – Diffusion bonding of metal alloys in aerospace and other applications. In: Chaturvedi, M.C. (Ed.), *Welding and Joining of Aerospace Materials*. Woodhead Publishing, pp. 320–344.
- Lesuer, D.R., Syn, C.K., Sherby, O.D., *et al.*, 1996. Mechanical behaviour of laminated metal composites. *International Materials Reviews* 41 (5), 169–197. doi:10.1179/imr.1996.41.5.169.
- Liu, B.X., *et al.*, 2013. Microstructure and tensile behavior of novel laminated Ti–TiBw/Ti composites by reaction hot pressing. *Materials Science and Engineering: A* 583, 182–187. doi:10.1016/j.msea.2013.06.058.
- Liu, B.X., Huang, L.J., Geng, L., *et al.*, 2014a. Fabrication and superior ductility of laminated Ti–TiBw/Ti composites by diffusion welding. *Journal of Alloys and Compounds* 602, 187–192. doi:10.1016/j.jallcom.2014.02.140.
- Liu, B.X., Huang, L.J., Wang, B., Geng, L., 2014b. Effect of pure Ti thickness on the tensile behavior of laminated Ti–TiBw/Ti composites. *Materials Science and Engineering: A* 617, 115–120. doi:10.1016/j.msea.2014.08.065.
- Liu, B.X., *et al.*, 2014c. Gradient grain distribution and enhanced properties of novel laminated Ti–TiBw/Ti composites by reaction hot-pressing. *Materials Science and Engineering: A* 595, 257–265. doi:10.1016/j.msea.2013.12.013.
- Liu, B.X., Huang, L.J., Rong, X.D., Geng, L., Yin, F.X., 2016. Bending behaviors and fracture characteristics of laminated ductile-tough composites under different modes. *Composites Science and Technology* 126, 94–105. doi:10.1016/j.compscitech.2016.02.011.
- Miracle, D.B., Pandey, A.B., Majumdar, B.S., 2001. Laminated particulate-reinforced aluminum composites with improved toughness. *Acta Materialia* 49 (3), 405–417. doi:10.1016/S1359-6454(00)00332-3.
- Monazzah, A.H., Bagheri, R., Reihani, S.M.S., 2013. Toughness enhancement in roll-bonded Al6061-15 vol% SiC laminates via controlled interfacial delamination. *Journal of Materials Engineering and Performance* 22 (11), 3414–3420. doi:10.1007/s11665-013-0626-8.
- Osman, T.M., Singh, P.M., Lewandowski, J.J., 1994. Crack bridging in a laminated metal matrix composite. *Scripta Metallurgica Materialia* 31 (5), 607–612. doi:10.1016/0956-716X(94)90152-X.
- Osman, T.M., Hassan, H.A., Lewandowski, J.J., 2008. Interface effects on the quasi-static and impact toughness of discontinuously reinforced aluminum laminates. *Metallurgical and Materials Transactions A* 39 (8), 1993–2006. doi:10.1007/s11661-008-9538-x.
- Partridge, P.G., Smith, D., Zuo, Y.Q., 1996. Comparative analysis of mechanical properties of laminates composed of layers of titanium alloy and titanium alloy metal matrix composite. *Materials Science and Technology* 12 (11), 923–927. doi:10.1179/mst.1996.12.11.923.
- Prikhodko, S.V., *et al.*, 2020. Diffusion bonding of TiC or TiB reinforced Ti–6Al–4V matrix composites to conventional Ti–6Al–4V alloy. *Science and Technology of Welding and Joining*. 1–7. doi:10.1080/13621718.2020.1751403.
- Qiang, Q., Xinghong, Z., Songhe, M., *et al.*, 2008. Reactive hot pressing and sintering characterization of ZrB2–SiC–ZrC composites. *Materials Science and Engineering: A* 491 (1), 117–123. doi:10.1016/j.msea.2008.01.053.
- Saito, Y., Utsunomiya, H., Tsuji, N., Sakai, T., 1999. Novel ultra-high straining process for bulk materials – Development of the accumulative roll-bonding (ARB) process. *Acta Materialia* 47 (2), 579–583.
- Salzar, R.S., 1999. Design considerations for rotating laminated metal-matrix-composite shafts. *Composites Science and Technology* 59 (6), 883–896. doi:10.1016/S0266-3538(98)00129-8.
- Shenoi, R.A., 1993. An engineering approach to the prediction of elastic properties of a laminate. In: Shenoi, R.A., Wellicome, J.F. (Eds.), *Composite Materials in Maritime Structures*, first ed. Cambridge University Press, pp. 127–141.
- Shirzadi, A., 2008. Chapter 9 – Solid-state diffusion bonding. In: Zhou, Y. (Ed.), *Microjoining and Nanjoining*. Woodhead Publishing, pp. 234–249.
- Sills, R.B., Thouless, M.D., 2015. Cohesive-length scales for damage and toughening mechanisms. *International Journal of Solids and Structures* 55, 32–43. doi:10.1016/j.ijsolstr.2014.06.010.
- Smith, D.J., Zuo, Y.Q., Partridge, P.G., Wisbey, A., 1997. Bend stiffness and strength of laminates composed of titanium alloy and titanium metal matrix composite. *Materials Science and Technology* 13 (1), 35–40. doi:10.1179/mst.1997.13.1.35.
- Syn, C.K., Lesuer, D.R., Sherby, O.D., 1996. Enhancing tensile ductility of a particulate-reinforced aluminum metal matrix composite by lamination with Mg-9%Li alloy. *Materials Science and Engineering: A* 206 (2), 201–207. doi:10.1016/0921-5093(95)09995-6.
- Syn, C.K., Stoner, S., Lesuer, D.R., Sherby, O.D., 1994. Influence of volume fraction of component materials and interlayer bond strength on fracture toughness of multi-layer Al 6090–25 vol% SiCp and Al 5182 laminates. In: *Proceedings of the Symposium on High Performance Metal and Ceramic Matrix Composites*. pp. 125–136.
- Tomida, S., Nakata, K., Saji, S., Kubo, T., 2001. Formation of metal matrix composite layer on aluminum alloy with TiC-Cu powder by laser surface alloying process. *Surface and Coatings Technology* 142–144, 585–589. doi:10.1016/S0257-8972(01)01172-0.
- Tsuji, N., Saito, Y., Utsunomiya, H., Tanigawa, S., 1999. Ultra-fine grained bulk steel produced by accumulative roll-bonding (ARB) process. *Scripta Materialia* 40 (7), 795–800. doi:10.1016/S1359-6462(99)00015-9.
- Wang, S., *et al.*, 2019. Regulating crack propagation in laminated metal matrix composites through architectural control. *Composites Part B: Engineering* 178, 107503. doi:10.1016/j.compositesb.2019.107503.

- Wang, S., Huang, L., An, Q., Geng, L., Liu, B., 2018. Dramatically enhanced impact toughness of two-scale laminate-network structured composites. *Materials & Design* 140, 163–171. doi:10.1016/j.matdes.2017.11.067.
- Weng, F., Chen, C., Yu, H., 2014. Research status of laser cladding on titanium and its alloys: A review. *Materials & Design* 58, 412–425. doi:10.1016/j.matdes.2014.01.077.
- Wong, P.K., Kwok, C.T., Man, H.C., Cheng, F.T., 2012. Chapter 8 – Laser surface alloying (LSA) of copper for electrical erosion resistance. In: Kwok, C.T. (Ed.), *Laser Surface Modification of Alloys for Corrosion and Erosion Resistance*. Woodhead Publishing, pp. 288–319.
- Wu, H., Fan, G., Jin, B.C., *et al.*, 2016. Fabrication and mechanical properties of TiBw/Ti-Ti(Al) laminated composites. *Materials & Design* 89, 697–702. doi:10.1016/j.matdes.2015.10.025.
- Wu, W.-W., Zhang, G.-J., Kan, Y.-M., Wang, P.-L., 2008. Reactive hot pressing of ZrB₂-SiC-ZrC composites at 1600°C. *Journal of the American Ceramic Society* 91 (8), 2501–2508. doi:10.1111/j.1551-2916.2008.02507.x.
- Xu, Q., Hayes, R.W., Hunt, W.H., Lavernia, E.J., 1998. Mechanical properties and fracture behavior of layered 6061/SiCp composites produced by spray atomization and co-deposition. *Acta Materialia* 47 (1), 43–53. doi:10.1016/S1359-6454(98)00340-1.
- Zhang, J., Lewandowski, J.J., 1997. Delamination study using four-point bending of bilayers. *Journal of Materials Science* 32 (14), 3851–3856. doi:10.1023/A:1018692110821.
- Zhang, W., Travitzky, N., Hu, C., Zhou, Y., Greil, P., 2009. Reactive hot pressing and properties of Nb₂AlC. *Journal of the American Ceramic Society* 92 (10), 2396–2399. doi:10.1111/j.1551-2916.2009.03187.x.
- Zhao, K.N., Xu, D.X., Li, H.X., Zhang, J.S., Chen, D.L., 2019. Microstructure and mechanical properties of Mg/Mg bimetal composites fabricated by hot-pressing diffusion and co-extrusion. *Materials Science and Engineering: A* 764, 138194. doi:10.1016/j.msea.2019.138194.
- Zuo, Y.Q., Smith, D.J., Partridge, P.G., 1998. Damping capacity of laminates composed of layers of titanium alloy and titanium alloy MMC. *Materials Science and Technology* 14 (6), 518–521. doi:10.1179/mst.1998.14.6.518.

Eco-friendly Metal Matrix Composites

Gururaj Parande, Vyasraj Manakari, and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composites (MMCs) are excellent suitors for application in weight critical applications owing to their high structural properties like elastic modulus, tensile strength, wear resistance, damping characteristics as compared to monolithic alloys. MMCs offer engineers value as they are especially suitable for uses requiring high-temperature stability and structural rigidity, lightweighting, and dimensional stability. The contemporary tendency is in the direction of safe application of the MMC parts in high pressure and temperature environments in aerospace and automobile engines. The development of MMCs reinforced with ceramic particles is a result of increased demand for stiff, strong, and lightweight materials.

High-performance lightweight cost-effective MMCs are gaining great importance in both structural and non-structural applications (Rohatgi, 1991; Kelly, 2006). MMCs studies have shown to have a significant improvement in properties and hence its potential application as compared to their monolithic counterpart. These MMCs can be specially designed to show high durability, ductility, tensile modulus, thermal conductivity, etc (Staiger *et al.*, 2006; Rawal, 2001; Shelley *et al.*, 2001). To improve its widespread acceptance in electronics, aerospace, robotics, and medical applications, special features can be incorporated in the design and development of MMCs (Ajayan *et al.*, 1993). Since the 1960s, the development of high strength carbon fibers resulted in their usage in missile conical tips, conical exit parts of the rocket, heat shields, etc. The commercial society, for the first time, noticed the importance of lightweight components exhibiting high strength properties for structural and non-structural applications as opposed to conventional alloys (Thostenson *et al.*, 2001).

The commitment by the world towards improving the sustainability of society is well documented by the Paris agreement (2015) in efforts to work towards arresting the catastrophes of climate change by reducing carbon dioxide emissions by 2 billion tons at the end of 2025 (Gupta and Gupta, 2017). To constantly innovate towards a sustainable future, as materials scientists, it is imperative to move towards making the process eco-friendly. MMCs need to be developed such that the materials find applications in cross-themed sectors like aerospace, automotive and biomedical sectors alike. Eco-friendly metal matrix composites can be realized by:

- (1) Using low-cost energy-efficient materials with high performance and widerpread applications
- (2) Using low-cost processing technology to fabricate these materials at a high volume scale
- (3) A combination of both.

In this article, the emphasis is on discussing the efforts of the research community so far in developing high-performance eco-friendly metal matrix composites. Aluminum and rare earth matrix composites are not discussed in this article as lately, several studies have reported that Al is neurotoxic, and the REs have been found to cause latent toxicity and several other harmful effects on the human body (Parande *et al.*, 2018b). Hence, substituting or reducing these elements with appropriate cost-effective bio-compatible elements and reinforcements is a sustainable option. Composites developed with zinc, titanium, and magnesium-based matrix are discussed in this article. The processing technologies commonly used in developing such composites are also briefly discussed. Mechanical, microstructural, corrosion, and tribological properties of the composites are summarized.

Processing Technologies for Eco-friendly Metal Matrix Composites

To process high-performance metal matrix composites effectively, the selection of efficient processing parameters is rendered highly valuable. The processing technologies are broadly classified into solid-state processing and liquid-state processing. In this section, the authors discuss the different methods of synthesizing eco-friendly metal matrix composites.

Solid-State Processing

Powder metallurgy: The powder metallurgy technique usually involves blending and/or mechanical alloying of the raw material powders in the required composition (Fig. 1). The matrix and reinforcements are mixed in the right amounts and the reinforcements are blended using a blender or high energy ball milling. The blended powders are then uniaxially compacted into green compacts. These green compacts exhibit a relative density of ~80%. Densification of these green compacts is done by sintering. Sintering can be performed using conventional sintering, resistance sintering, or microwave sintering (Gupta and Leong, 2008). Mechanical alloying is capable of synthesizing a variety of high strength equilibrium and non-equilibrium alloys due to the high dislocation density and homogenous distribution of reinforcing constituents.

Additive manufacturing: Additive manufacturing (AM) is used to create parts layer-by-layer. It is also called 3D printing, rapid manufacturing or rapid prototyping, or solid freeform fabrication. This technique enables the development of highly complex and

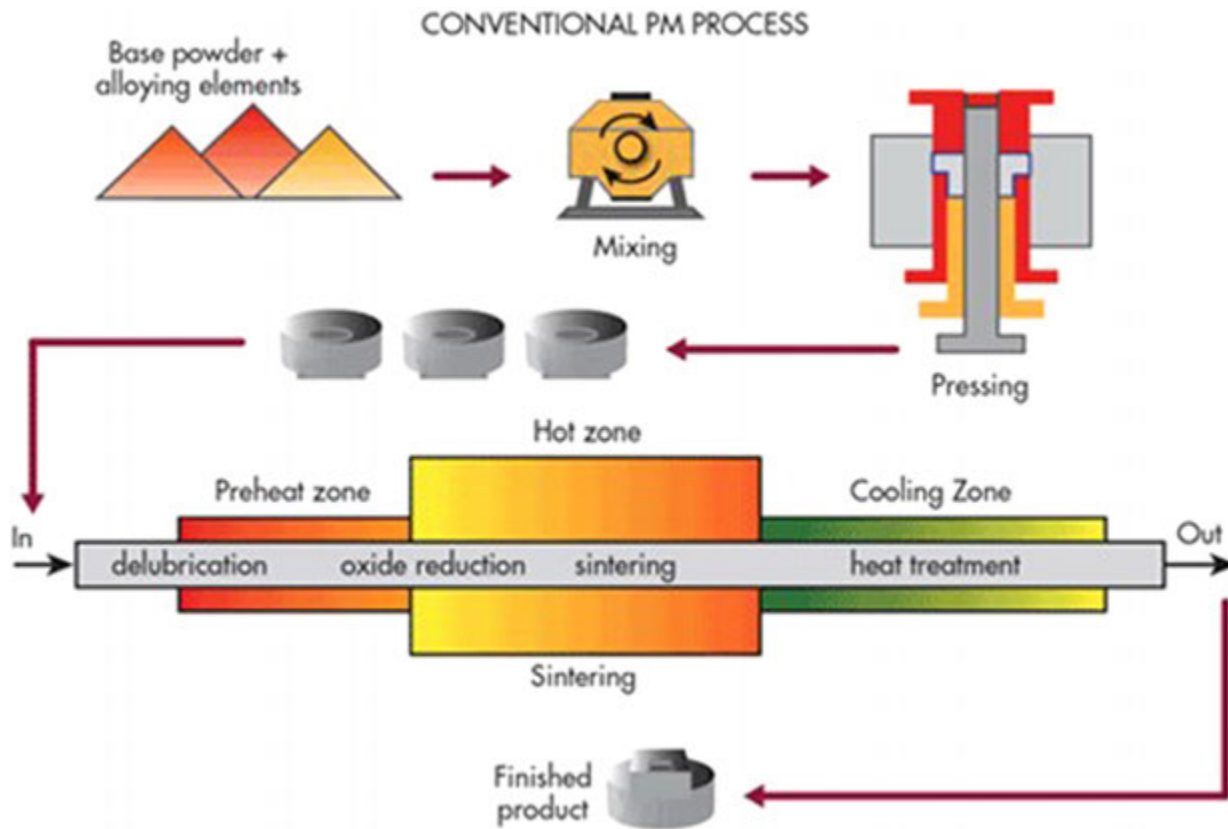


Fig. 1 Schematic of the process for preform fabrication by the powder metallurgy process. Reproduced from Kerns, J., 2016. Powder-metallurgy processes. Machine design, pp. 1–5.

intricate physical shapes and sizes assisted by Computer-Aided Design (CAD) systems. The model generated using CAD software is sliced into many layers with every layer defined by layer thickness and the object is built in a layer-by-layer fashion. Additive manufacturing technology to synthesize magnesium-based alloys and composites has gained high notice in the last 5–7 years. Some of the techniques used to develop metal-based alloys and composites are: (1) selective laser melting, (2) inkjet printing, (3) laser sintering, (4) laser powder deposition, (5) electron beam melting, and (6) wire-based additive manufacturing (Salehi *et al.*, 2018). Although AM offers an exciting avenue to develop novel metallic materials, the strength properties reported by these parts are still lower than commercially used alloys. Hence, a high level of optimization is required to make these components more viable.

Following the primary processing as mentioned above, the composites can be subjected to several secondary processing routes such as extrusion, rolling, or forging (Tekumalla *et al.*, 2016; Itoi *et al.*, 2008; Malaki *et al.*, 2019) to further consolidate or shape the composite materials to tailor them as per the requirement. Schematic of a powder bed additive manufacturing process can be seen below in Fig. 2.

Liquid State Processing

Sand casting: Sand casting is a commonly used liquid processing method to develop metal-based components and parts. The material to be cast is processed by pouring the molten slurry into a sand mold cavity. On cooling the mold, the slurry solidifies, and the cast material is released from the mold. In order to achieve high-quality cast products, it is important to reduce the mold-molten metal reactions as some metals like magnesium are highly reactive at elevated temperatures and may react with the sand (Avedesian and Baker, 1999). This can be achieved by (1) reducing the content of moisture in the sand and (2) incorporating suitable inhibitors like sulfur, potassium fluoroborate, boric acid, individually or in combination, to make the core and the molds.

Die casting: Die casting is also known as high-pressure die casting. During this process, the molten slurry is channeled through a narrow gate to fill up the mold cavity at an expedited rate (Malaki *et al.*, 2019). During solidification, a significant high pressure in the range of 40–1000 MPa is applied to the melt. This is to ensure no gas entrapments and melt is compressed and shrinkage of the metal part is reduced. The cast part solidifies at a very high cooling rate (10–1000°C/s) resulting in a refined microstructure. Die casting is commonly used for producing near net-shaped products. A schematic of the low-pressure die casting (LPDC) setup is shown in Fig. 3.

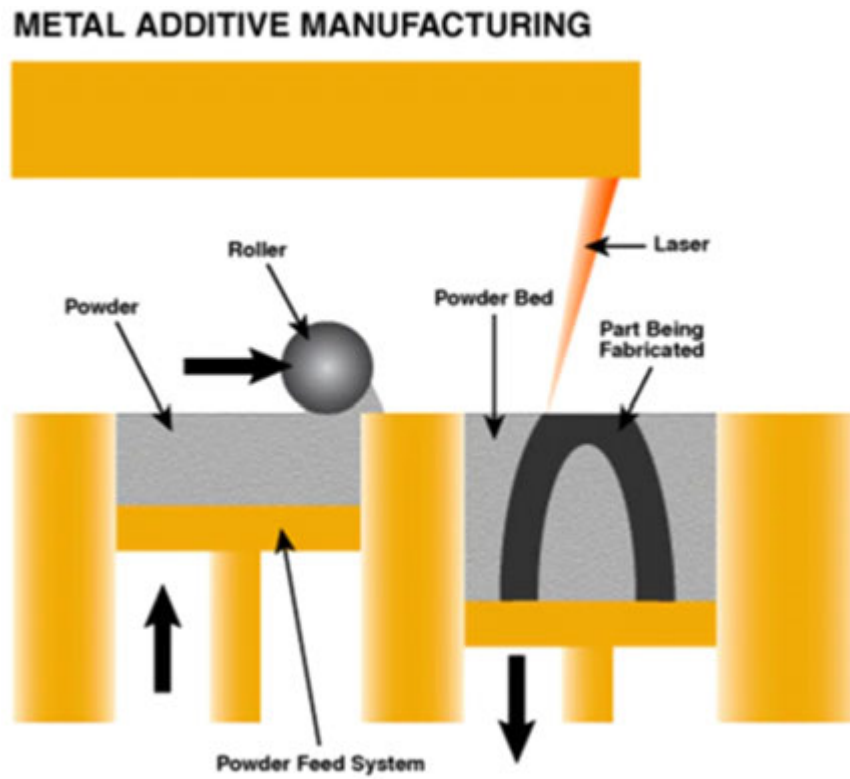


Fig. 2 Schematic of the powder bed additive manufacturing process. Reproduced from Kerns, J., 2016. Powder-metallurgy processes. Machine design, pp. 1–5

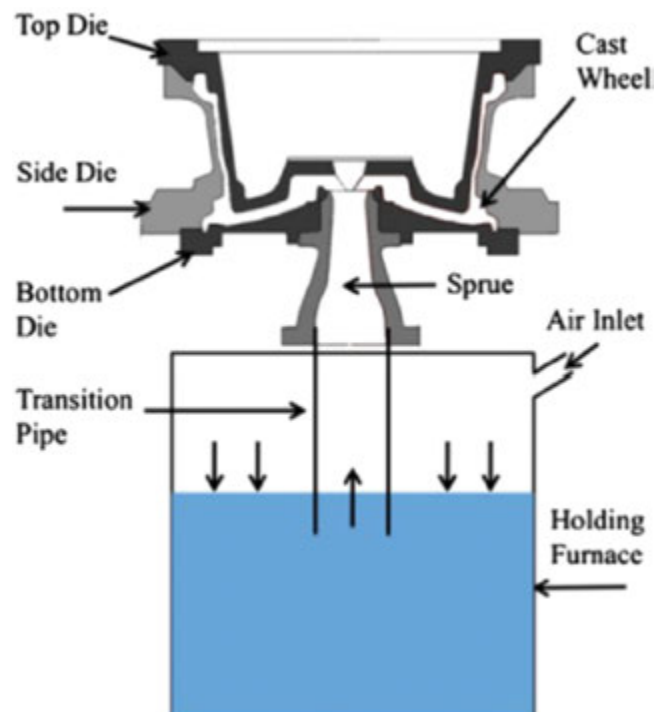


Fig. 3 Schematic showing the basic structure of the LPDC process. Reproduced from Duan, J., 2016. Development of a Numerical Optimization Methodology for the Aluminum Alloy Wheel Casting Process. University of British Columbia.

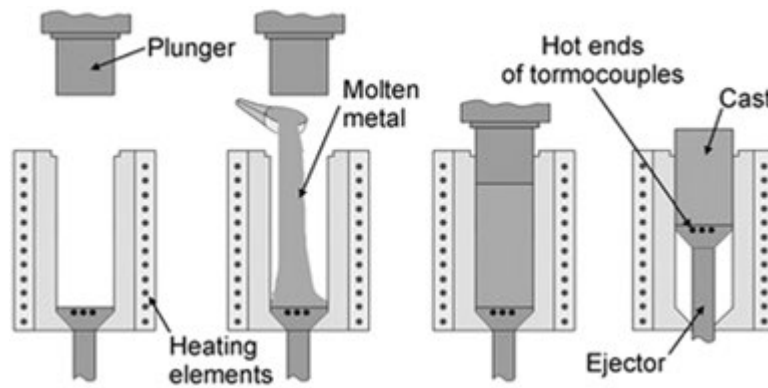


Fig. 4 Schematic diagram of the squeeze casting process. Reproduced from Klasik, A., Pietrzak, K., Makowska, K., *et al.*, 2016. Wear resistance of aluminum matrix composites reinforced with Al_2O_3 particles after multiple remelting. *Journal of Materials Engineering and Performance* 25 (8), 3084–3090.

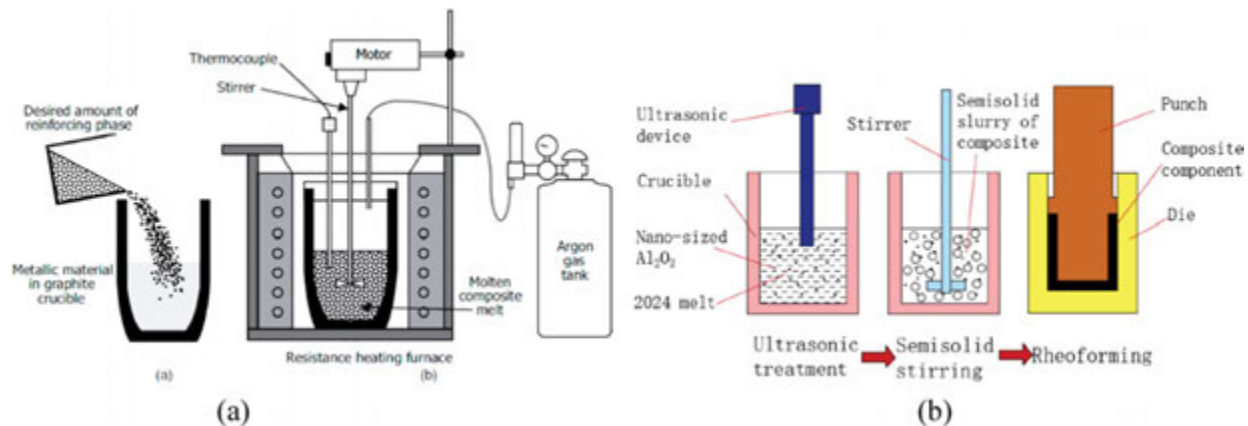


Fig. 5 (a) A typical schematic representation of a stir casting setup (b) schematic diagram of fabricating and rheoforming the semisolid slurry of the metal matrix composite. Reproduced from (a) Malaki, M., Xu, W., Kasar, A.K., 2019. Advanced Metal Matrix Nanocomposites, *Metals* 9 (3), 330. (b) Jiang, J., Xiao, G., Che, C., Wang, Y., 2018. Microstructure, Mechanical Properties and Wear Behavior of the Rheoformed 2024 Aluminum Matrix Composite Component Reinforced by Al_2O_3 Nanoparticles, *Metals* 8 (6), 460.

Squeeze casting: Squeeze casting is a combination of the casting and forging processes as shown in Fig. 4. There are two types of squeeze casting namely: (1) direct squeeze casting and (2) indirect squeeze casting.

Direct squeeze casting, also known as a metal forging (Gupta and Ling, 2011), is a process when the molten slurry is poured into the lower half of the die and the upper die is lowered to complete the die set. The metallic slurry solidifies under the action of high unidirectional pressure to form the cast ingot. This technology is widely used for the processing of metal matrix composites, mainly particle reinforced metal matrix composites.

Indirect squeeze casting, though similar to direct type, but has huge similarity to the die casting method wherein the molten metal is introduced into the sleeve of the squeeze casting equipment. By optimizing the speed of the plunger, the speed at which the molten slurry is filled in the die can be manipulated. In order to achieve high dense castings, the filling speed of the molten slurry must be controlled to circumvent any turbulent flow. This method is suitable to produce metal matrix composites although the material yield in this type is not as high as the direct type.

Stir casting: Stir casting is a three-step process that involves (Malaki *et al.*, 2019): (1) melting of the matrix material, (2) incorporation of the alloying element/secondary reinforcement into the molten metal, and (3) optimized stirring to achieve uniform distribution of the reinforcements in the matrix (Fig. 5(a)). This molten slurry is then transferred to a casting setup like sand/die/mold casting. Stir casting is traditionally used for materials with a high volume of secondary reinforcements (10%–30%).

Spray forming: Spray forming is a technique also known as spray atomization and deposition or spray casting or Osprey process (Gupta and Ling, 2011). It is used to produce near net-shaped parts. In this process, the pure metal or alloy is melted in a resistance/induction furnace. The reinforcement is added either inside or outside the crucible into the molten spray. The melt/slurry is homogenized to achieve uniform distribution of secondary phases before pouring. An agitator in the form of a mechanical stirrer is sometimes used for mixing. The molten slurry/melt is then released as a free-falling stream and impacted by high energy inter gas or water jets thereby atomizing the melt onto the substrate and a preform is developed.

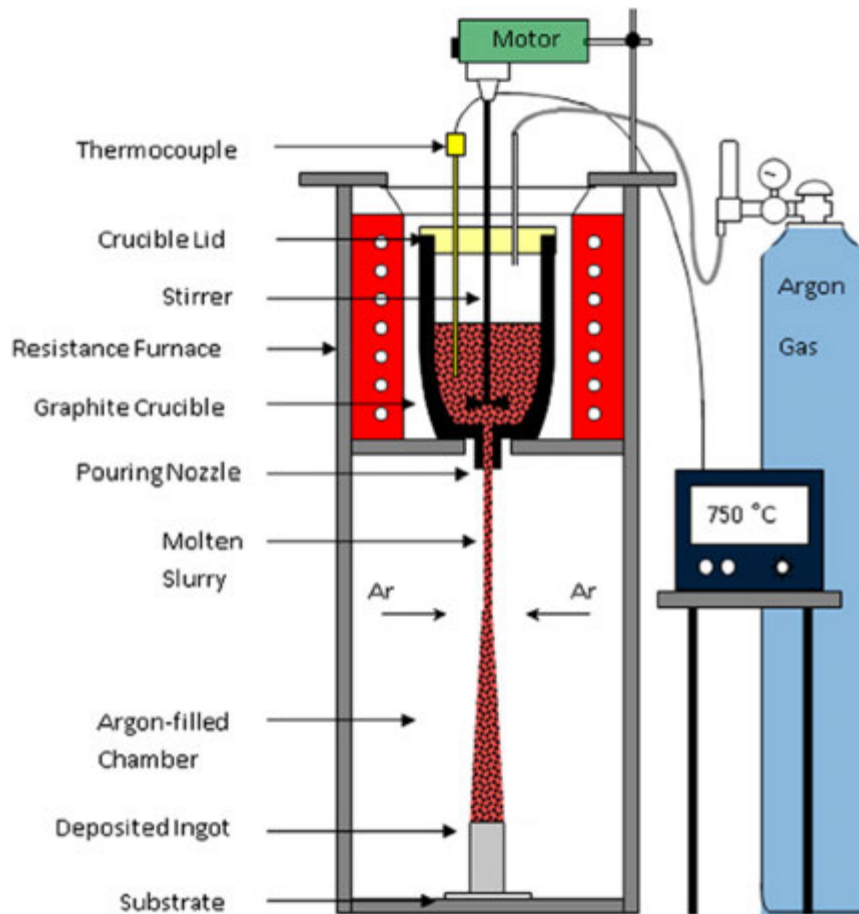


Fig. 6 Schematic representation of the DMD setup. Reproduced from Malaki, M., Xu, W., Kasar, A.K., 2019. Advanced Metal Matrix Nanocomposites, *Metals* 9 (3), 330.

Semi-solid casting: SSM casting is also known as thixomolding, rheocasting, thixocasting, or thixoforming (Fig. 5(b)). The thixomolding process is similar to plastic injection molding. The raw material is heated to a temperature just below the melting point under a protective argon atmosphere. Heating is done by a rotating screw and hence forms the slurry. This molten slurry is injected into the die at higher speeds to obtain the cast part. Rheocasting is a process where the raw material is heated in a mushy zone followed by die casting. In the case of metal matrix composites, reinforcements are added at the semi-solid temperature, the molten slurry is stirred, and the part is die-casted.

Melt infiltration: This process involves the infiltration of molten metal or alloy in a preform in either absence or presence of external pressure. Preparation of reinforcement into porous preform follows the injection of molten metal into the reinforcement preform (Sravva, 2018). The metal infiltrates through the open pores of the reinforcement to form a composite. Pressurized infiltration involves the application of some pressurizing medium such as gas or mechanical device. Controlling appropriate pressure during injection is important as relatively higher pressures can damage the reinforcement. This process can also be used to produce composites containing a higher volume fraction of reinforcements (40%–50%). Some of the limitations are the damage of reinforcements due to higher injection pressure, microstructural coarsening, and the formation of interfacial reaction products.

Disintegrated melt deposition: Disintegrated melt deposition (DMD) technique was developed in the early 1990s. A schematic diagram of the DMD technique representative of its actual setup developed at the National University of Singapore is shown in Fig. 6 (Gupta and Wong, 2015). DMD is a unique technique that brings together the cost-effectiveness associated with the conventional casting process and the scientific innovativeness and technological potential associated with the spray forming process. However, unlike spray forming, the DMD technique uses low to moderate superheat temperatures and lower impinging gas jet velocity. Within a graphite crucible, the metal along with alloying elements or reinforcements are superheated to 750°C under an argon gas atmosphere using a resistance heating furnace. For achieving a homogeneous metal matrix, the superheated slurry is stirred at 465 rpm for 5–10 min using a twin-blade with a pitch of 45°. ZIRTEX 25 (86% ZrO₂, 8.8% Y₂O₃, 3.6% SiO₂, 1.2% K₂O and Na₂O, and 0.3% trace inorganic) coating is applied on the stirrer to avoid iron contamination of the molten metal. After stirring, the molten metal is bottom poured into the mold, under the influence of gravity, through a 10 mm hole in the crucible. Before entering the mold, the molten metal is disintegrated by two jets of argon gas oriented normal to the melt stream.

The flow rate of argon is maintained at 25 l/min and an ingot of 40 mm diameter (variable and as required) is normally obtained. The ingot obtained is then machined to the desired length as required by the secondary processing method.

Properties for Eco-friendly Metal Matrix Composites

In this section, the microstructure and various properties like mechanical, tribological and corrosion properties of the eco-friendly metal matrix composites are discussed. The discussion is segregated based on the matrix (Zn, Ti, and Mg) and the reported advancements in the literature are highlighted.

Zinc Matrix Composites

Zinc casting alloys are versatile engineering materials. They provide an attractive combination of toughness, rigidity, strength, economical castability, and bearing and sliding wear performance. Also, zinc alloys can be synthesized at lower costs and lower casting temperatures (Owoeye *et al.*, 2019). Zinc plays an important role as a structural protein component, enzymatic cofactor, and is a vital trace element for human health acting as a transcriptional regulator in a wide range of cellular and biochemical activities (Solomons, 2013). More notably, zinc is engaged significantly in bone formation and resorption. The research on Zn being used as a potential orthopedic implant had not been reported in the literature until recently. It was recently reported in a study that the degradation rate of pure Zn is slow; it may take more than a decade for a 5 mm diameter pure Zn screw to degrade completely under bone environments (Yang *et al.*, 2018). Zinc-based composites with high mechanical strength and enhanced corrosion resistance are important for their widespread use in the orthopedic sector.

Zinc–aluminum (ZA) alloys can provide energy and economically conscious alternatives for a range of ferrous and non-ferrous alloys due to their excellent wear resistance, lower casting temperature, high strength, and abundant ability (Owoeye *et al.*, 2019).

ZA-27 alloy containing 26%–28% Al, 2%–2.5% Cu, and 0.01%–0.02% Mg was initially developed as a high strength gravity casting alloy and is widely being exploited as materials for bushings and bearings operating at low-speeds and high loads, primarily in drive trains, automobiles, wear plates and thrust washers (Sharma *et al.*, 1998). Hard secondary phases/reinforcements, such as alumina (Al_2O_3), silicon carbide (SiC), graphite, and zirconia (ZrO_2) have been effectively used as a whole or to form a hybrid, resulting in a massive property augmentation to improve the hardness, elastic modulus, strength, and wear resistance of ZA-27 alloy. However, properties like machinability, damping capacity, corrosion resistance, impact resistance, and fracture toughness (Owoeye *et al.*, 2019). However, due to the modern endeavors geared towards designing low-cost high-performance metal matrix composites, industrial waste particles and agro-waste ashes (Alaneme *et al.*, 2013; Madakson *et al.*, 2012) have been used as reinforcement to supplement either in part or wholly instead of high-cost synthetic reinforcement materials, such as SiC and alumina in ZA-27 composites (Fatile *et al.*, 2015; Folorunso and Owoeye, 2019; Almomani *et al.*, 2017; Miloradovic and Stojanovic, 2013; Kiran *et al.*, 2013; Alaneme and Ajayi, 2017).

Microstructure

Several authors in recent years, the microstructural characteristics of ZA-27 MMCs with synthetic ceramics dispersoids in combination with agro or industrial wastes have been explored and published (Fatile *et al.*, 2015; Folorunso and Owoeye, 2019; Almomani *et al.*, 2017; Miloradovic and Stojanovic, 2013; Kiran *et al.*, 2013; Alaneme and Ajayi, 2017). As stated by these studies, monolithic ZA-27 alloy is typically characterized by a dendritic pattern (a feathery feature) displaying the solidification pattern and grain morphology and composed of dendrites of primary Al-rich phase (α , FCC) generally designated by a white pattern and an inter-dendritic zinc-rich phase (η , HCP) ordinarily showed by the dark area, while the zone surrounding the α -phase is a combination of $\alpha + \eta$ area (Figs. 7–8). Although, in the case of most ZA-27 MMCs, the secondary phase particles have been described to show high interfacial integrity with the matrix despite high thermal expansion coefficient mismatch leading to high residual thermal stresses. Further, the uniform distribution of the reinforcement phase is observed in the metal matrix with limited agglomerations.

Mechanical properties

BhaskarRaju *et al.* (2017) studied the mechanical properties of ZA-27 reinforced with (0, 3, 6, and 9 wt%) SiC and reported a substantial improvement in the hardness, impact strength, compressive strength, and tensile strength of the ZA-27/SiCp composites with progressive addition of SiC.

Dalmis *et al.* (2016) investigated the effect of graphite (Gr) nanoparticles on the mechanical and physical properties of ZA-27 alloy. The authors concluded that the tensile strength and hardness decreased with the increased presence of Gr content in the alloy. This behavior was attributed to poor wettability between the ZA-27 matrix alloy and Gr particles.

Ranganath *et al.* (Owoeye *et al.*, 2019) studied mechanical properties and fracture characteristics of ZA-27/TiO₂ MMCs containing particles in the range from 0 to 6 wt% and showed significant improvements in hardness, yield strength, ultimate tensile strength, and elastic modulus albeit at the expense of fracture strain properties.

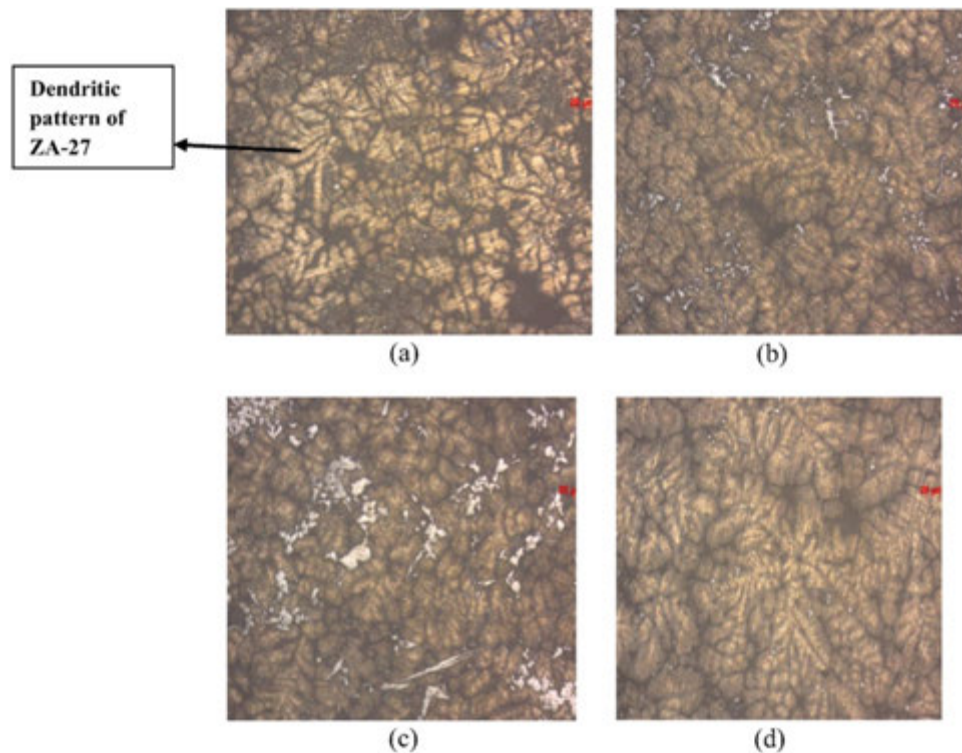


Fig. 7 (a) Representative micrograph showing: (a) unreinforced ZA-27 alloy (b) 100% SiC_p reinforced ZA-27, (c) 50% QD: 50% SiC_p hybrid ZA-27, (d) 75% QD: 25% SiC_p hybrid ZA-27. Reproduced from Folorunso, D.O., Owoeye, S.S., 2019. Influence of quarry dust-silicon carbide weight percentage on the mechanical properties and tribological behavior of stir cast ZA-27 alloy based hybrid composites. *Journal of King Saud University-Engineering Sciences* 31 (3), 280–285.

Sharma *et al.* (1996) studied the impacts of short glass fibers (0–5 wt%) on the mechanical response of cast ZA-27 alloy composites and reported a significant improvement in the elastic modulus, hardness, and the ultimate tensile strength an increased amount of reinforcement. However, the impact resistance and tensile ductility showed adverse behavior.

Alaneme *et al.* (2016) studied the wear and mechanical behavior of (5, 7.5, and 10 wt%) steel chips reinforced ZA-27 composites. It was stated that the composites displayed improved hardness and wear resistance with the increased addition of the steel chips from 5 to 10 wt%. However, a strength decrement was observed to a non-uniform dispersion and agglomeration of steel chips above 5 wt%.

Kiran *et al.* (2013) studied the mechanical properties of ZA-27/3Gr/(0–9 wt%)SiC_p hybrid composites for bearing applications. It was concluded that increased SiC_p content improved the ultimate tensile strength (UTS) of the composites. Also, noticeable enhancements were observed in the ultimate strength with the incorporation of 9 wt% SiC_p to ZA-27 (Fig. 9). The tensile strength and hardness enhanced by 11.2% with the presence of SiC_p from 0 to 5 wt% with observable decreased ductility properties.

Davies *et al.* (Folorunso and Owoeye, 2019) probed the effect of hybrid silicon carbide (SiC_p)-quarry dust (QD) on the strength and wear response of ZA-27-alloy containing 8 and 10 wt% QD-SiC_p with a varying amount of quarry dust (QD) from 0%, 25%, 50%, 75%, 100%, respectively. It was concluded that the tensile strength and hardness of the composites increased indicating a like trend as QD increased to the highest addition of 75% for both 8 and 10 wt% composites. Improved wear characteristics were observed for hybrid composites in comparison with the ZA-27-alloy with the presence of both SiC_p compositions.

Alaneme *et al.* (2014) studied the tensile and corrosion properties of Zn-27Al-based composites reinforced with silicon carbide (SiC_p) and bamboo leaf ash (BLA) containing 7 and 10 wt% BLA-SiC_p with wide-ranging amounts of 0%, 20%, 30%, and 40% BLA content, respectively. It was concluded that the tensile properties and hardness decreased with an increase in the wt% of BLA with no effect on ductility (Table 1). The reduction in hardness and tensile strength properties can be attributed to the presence of SiO₂ in BLA, which is known to be softer than SiC_p.

Kubásek *et al.* (2019) synthesized 5 wt% Mg containing Zn-Mg composite was synthesized using powder metallurgy and hot extrusion process. The presence of Mg in Zn improved the yield and ultimate strengths in both tensile and compressive modes significantly. The elongation under tensile mode however decreased from 35% to 16%.

Li *et al.* (Li, 2014) synthesized in-situ TiB₂ particles reinforced ZA27 and studied the effect on the hardness and tensile strength response. The presence of 2 wt% TiB₂ improved the ultimate tensile strength from 393 to 489 MPa, respectively. The Brinell hardness measurement also improved from 116 to 157 kgf/mm², respectively. Homogenous distribution of in-situ formed TiB₂

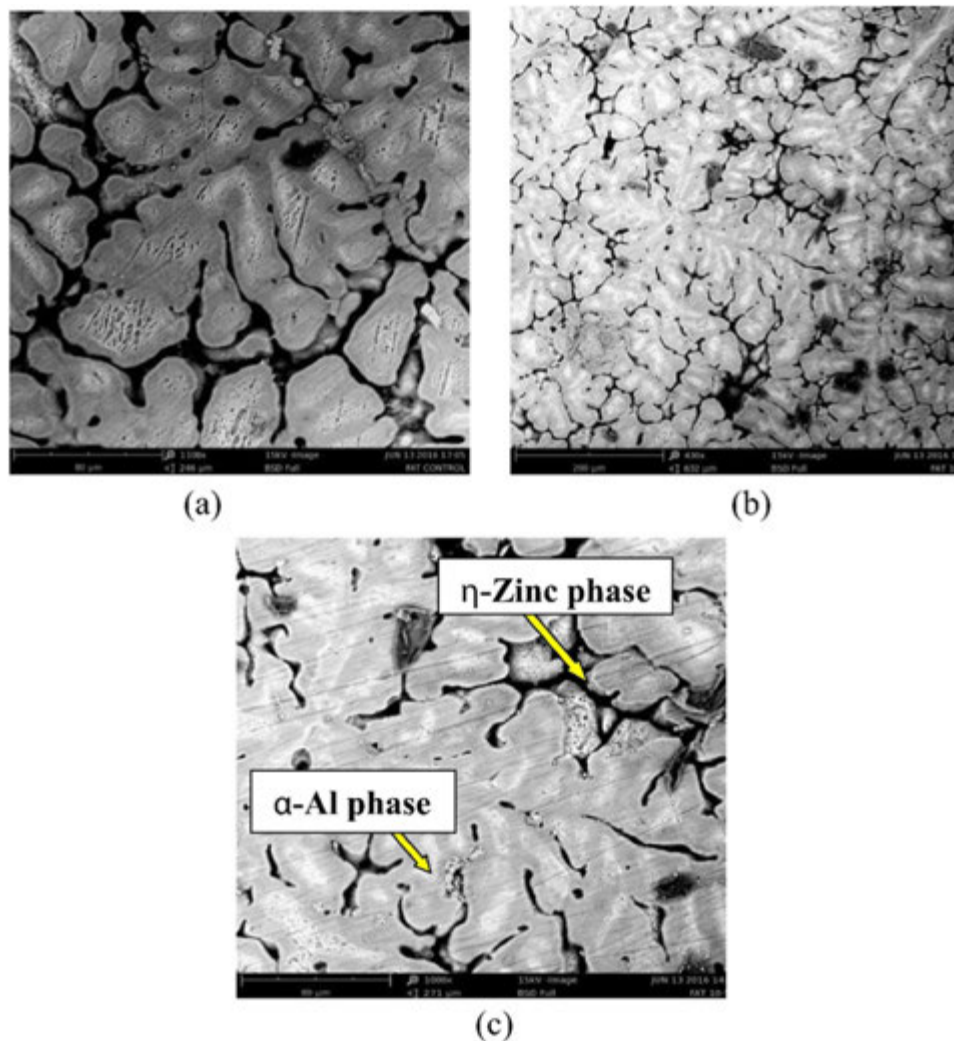


Fig. 8 Representative SEM images showing: (a) unreinforced ZA-27 alloy (b) 100% SiC_p reinforced ZA-27, (c) 50%QD: 50% SiC_p hybrid composite. Reproduced from Folorunso, D.O., Owoeye, S.S., 2019. Influence of quarry dust-silicon carbide weight percentage on the mechanical properties and tribological behavior of stir cast ZA-27 alloy based hybrid composites. *Journal of King Saud University-Engineering Sciences* 31 (3), 280–285.

particles was observed in the interdendritic regions between the primary α -Al dendrites in ZA27 alloy. The primary α -Al and η -Zn phase morphology and the amount of eutectoid structure varied considerably with the presence of TiB₂ particles.

Corrosion properties

Corrosion behavior of the ZA-27 alloy has been recently investigated by researchers (Barnhurst and Beliste, 1992; Porter, 1994). The ZA-27 alloy displays high corrosion resistance in natural atmospheres, soil, and waters, etc. as an effect of the capability of zinc to form protective oxide and hydroxide layers or their mixtures on the surface (Barnhurst and Beliste, 1992; Porter, 1994). However, more recently, several authors have studied and reported the effect of reinforcement particles on the corrosion characteristics of ZA-27 alloy (Almomani *et al.*, 2017; Alaneme *et al.*, 2014; Sharma *et al.*, 2001; Seah *et al.*, 1997; Pathak and Pandey, 2020).

Mohammed *et al.* (Almomani *et al.*, 2017) studied the corrosion behavior of Al₂O₃ and fly ash reinforced ZA-27 alloy in 3.5 wt% NaCl solution using direct current polarization test. It was reported that reinforcing ZA-27 alloy by Al₂O₃ and fly ash particles decrease its corrosion resistance. This behavior was attributed to the micro-galvanic corrosion occurring at the reinforcement level in the matrix.

Alaneme *et al.* (2014) also investigated the effect of silicon carbide (SiC_p) and bamboo leaf ash (BLA) on the corrosion behavior of ZA-27 alloy by immersion method in solutions of 0.3 M H₂SO₄ and 3.5 wt% NaCl. The presence of BLA-SiC_p in ZA-27 alloy realized a very stable response in 3.5 wt% NaCl solution and the corrosion resistance in 0.3 M H₂SO₄ solution was superior to that of the single SiC_p reinforced ZA-27 composite grade.

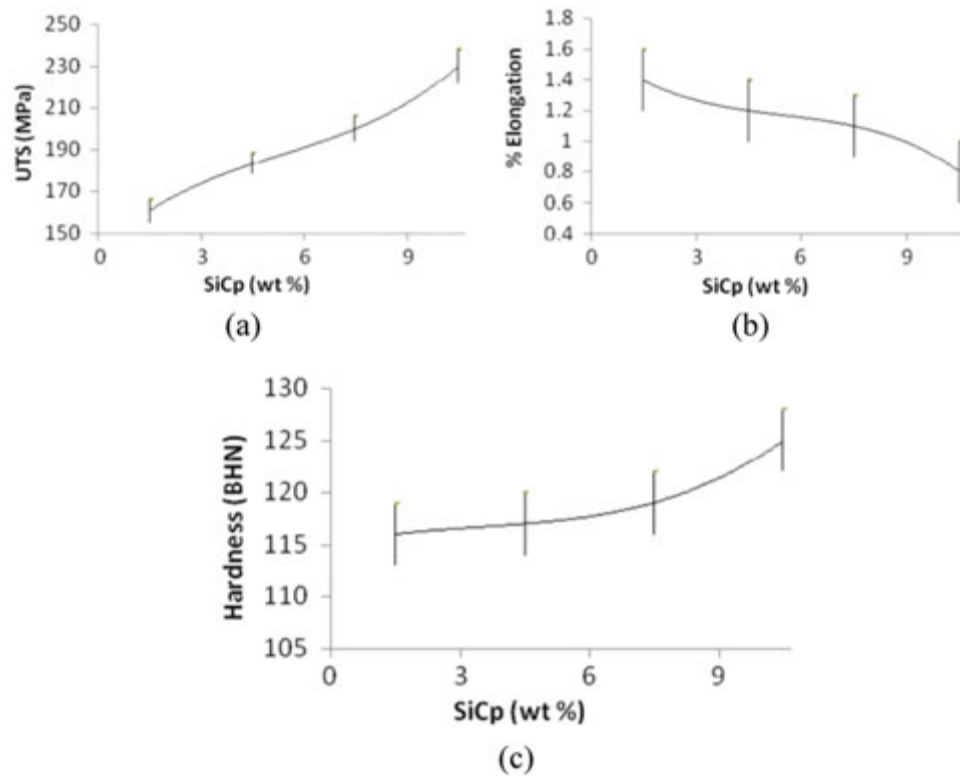


Fig. 9 Variation of (a) UTS, (b) elongation, and (c) hardness of ZA-27/3Gr material for different percentages of SiCp. Reproduced from Kiran, T., Kumar, M.P., Basavarajappa, S., Vishwanatha, B., 2013. Mechanical properties of as-cast za-27/gr/sicp hybrid composite for the application of journal bearing. *Journal of Engineering Science and Technology* 8 (5), 557-565.

Table 1 Mechanical properties Zn27Al-based composites

Sample designation	BLA (%)	UTS (MPa)	EI (%)	HRC
7 wt%				
A0	0	273.2	6.55	26.2
A20	20	269.7	6.7	25.6
A30	30	266	6.9	24.7
A40	40	258	6.2	23.4
10 wt%				
A0	0	316.8	6.3	28.3
A20	20	310.2	6.4	27.4
A30	30	292.4	6.5	26.7
A40	40	283.7	6.1	25.8

Note: Alaneme, K., Fatile, B., Borode, J., 2014. Mechanical and corrosion behaviour of Zn-27Al based composites reinforced with groundnut shell ash and silicon carbide. *Tribology in Industry* 36 (2).

Sharma *et al.* (2001) studied the effects of (1–5 wt%) particles on the corrosion characteristics of ZA-27 alloy in the HCl solution at room temperature using a conventional weight-loss method. It was concluded that the corrosion protection of the composites was enhanced with the progressive content of ZrSiO₄ particles. However, it was noted that the rate of corrosion was high owing to the pit formation ZA-27 alloy surface. However, in the composites, the pit formation occurred at the ZrSiO₄/ZA-27 interface.

Sharma *et al.* (Seah *et al.*, 1997) evaluated the corrosion characteristics of ZA-27/glass fibers in the HCl solution and observed that the higher the amount of glass fibers in the ZA-27 alloy, the higher is the corrosion protection. This is attributed to the inertness of the glass fibers. The chloride solution although destabilizes the formation of a protective layer due to the presence of active chloride ions causing anodic dissolution.

Pathak *et al.* (Pathak and Pandey, 2020) synthesized Fe containing Zn-based HAP composites and studied the corrosion and biocompatibility behavior of the materials. The progressive addition of HAP along with Fe in the Zn matrix leads to reduced

corrosion protection owing to the pit formation on the surface and micro galvanic corrosion. The cell viability studies of these composites displayed elongated shape of the cells revealed that the Zn based composites are highly non-toxic. The highest cell viability was observed in Zn-3HAP samples from indirect cytotoxicity evaluation.

Titanium Matrix Composites

Titanium and its alloys are rapidly becoming of substantial research importance for a broad range of products in the aerospace, automotive, and defense industries. These lightweight materials are lightweight to have salient properties such as excellent chemical resistance, high specific strength, and excellent biocompatibility. The holistic blend of these properties makes Ti-based alloys a viable option for chemical, marine, petrochemical, structural, and biomedical applications (Welsch *et al.*, 1993; Hayat *et al.*, 2019). However, the high-temperature resistance, wear-resistance, and elastic modulus of Ti-based materials are inferior to those of ferrous and Ni-based alloys (Li *et al.*, 2013; Kuzumaki *et al.*, 2000). Titanium metal matrix composites (TMMCs) provide an alternative to overcome these shortcomings.

The introduction of TMMCs into high-performance commercial sectors has not been forthright owing to the various complications involved in the design and development associated with high raw material and operating costs. Even so, steady attempts have been made by various researchers, particularly by the National Aeronautics and Space Administration (NASA), to improve their applicability for industrial usage. Among many success stories associated with TMMCs, the formation of the Titanium Matrix Composite Turbine Engine Composite Consortium (TMCTECC) program was a great attempt, where six US corporations collaborated for the design, development, and application of TMMCs into large gas turbine engines (Singerman *et al.*, 1996; Anderson, 1998).

In the titanium metal matrix composite technology, ceramic particles such as ZrC, TiB, TiB₂, B₄C, TiC, TiN, SiC, CNTs, and Al₂O₃. Among these TiB and TiC are most widely utilized (Geng *et al.*, 2008; Morsi and Patel, 2007). Apart from TiB and TiC, other reinforcements such as Si₃N₄ (Dougherty *et al.*, 2016), SiC (Sivakumar *et al.*, 2017), Al₂O₃ (Shivakumar *et al.*, 2015), and CNTs (Munir *et al.*, 2015) have also been reported in the public domain. A few interesting results are discussed in this section.

Mechanical properties

If the intrinsic properties of the matrix and the reinforcement are known, the stiffness and strength properties of the composites can be predicted in the longitudinal direction by the rule of mixtures, generally for the fiber-reinforced composites. The tensile strengths of TMMCs containing SiC reinforcement have been evaluated by some researchers fabricated by various processing methods. The effect of varying amounts of SiC fibers has also been studied (MacKay *et al.*, 1991; Pank and Jackson, 1993; Lobley and Guo, 1999; Leyens *et al.*, 2003; Leucht and Dudek, 1994).

Cui *et al.* (2018) studied graphene coated carbon fibers reinforced TiAl alloy composite fabricated by melt-spun, powder metallurgy, and vacuum melting. The work concluded that the composites showed excellent mechanical response with a hardness, fracture strain, and strength value of 426 HV, 26.27%, and 2312 MPa, respectively. It can be predicted that this methodology opens up novel prospects to synthesize TMMCs containing fibers in a simple yet unique manner.

According to the work in the public domain (Geng *et al.*, 2008; Morsi and Patel, 2007), in-situ synthesized TiC particulates (TiCp) and TiB whiskers (TiBw) and are known to be the effective reinforcements for directionally reinforced titanium composites (DRTC). This is owing to their similar density and thermal expansion coefficients and good chemical compatibility with titanium, high hardness, and high modulus. DRTCs display higher tensile properties than unreinforced Ti alloys over a range of temperatures. The ultimate tensile strength is increased owing to the distribution of fine whiskers and particulates leading to the dispersion-strengthening and hardening. The reinforcements restrict the dislocation movement, also known as the Orowan strengthening mechanism. In comparison with the precipitation hardening, the reinforcements added ex-situ added are observably stable at higher temperatures.

Recent articles in the literature (Chaudhari and Bauri, 2018; Choi and Kim, 2013; Kim *et al.*, 2011) suggest using different combinations of secondary reinforcements to realize the cumulative effects of individual reinforcements. Liu *et al.* (2015) designed and developed Ti64 alloy reinforced with Ti₃SiC₂ bar, ultrafine Ti₅Si₃ needle, and in-situ TiC particle composites. The study observed a tailored distribution of the secondary reinforcements. This was possible with larger sized matrix powders and smaller sized secondary reinforcement powders using low-energy milling, and an in-situ hot pressing process. In comparison with monolithic Ti64 alloy, the (Ti₃SiC₂ + Ti₅Si₃ + TiC)/Ti64 composites displayed an excellent combination of mechanical strength and fracture strain. The composites containing 5.0 vol% reinforcements with 0.5 μm-sized SiC displayed a UTS and fracture strain of 1171 MPa and 5.3%, respectively. This improvement in properties was attributed to the solid solution strengthening effect, strengthening due to the presence of hybrid reinforcements, a tailored network structure and, the large area of the Ti64 matrix. Table 2 provides a summary of the titanium matrix eco-friendly composites based on mechanical properties.

Tribological properties

Another area where discontinuously reinforced titanium matrix composites are the ideal option over composites containing fibers are applications requiring higher wear resistance. However, owing to their low hardness, Ti and its composites are generally considered not the preferred choice for wear-resistant applications. The presence and progressive addition of hard ceramics in the

Table 2 Mechanical properties of titanium matrix composites reported in the literature

Base matrix	Reinforcement	Processing technology	Strength (MPa)	Elongation (%)	References
Ti	5% TiB	VAR + HS	787	12.5	(Tsang <i>et al.</i> , 1997)
	15% TiB		903	0.4	
	40% TiB	SHS/PHIP	140		(Xinghong <i>et al.</i> , 2003)
	50% TiB		224		
	60% TiB		280		
	70% TiB		248.8		
	80% TiB		207		
	100% TiB		103		
	35% SiC fiber	MS	1163		(Bettge <i>et al.</i> , 2007)
	8–10% C fiber	PM	674		(Geng <i>et al.</i> , 2004)
	TiB and TiC	RHP	1190		(Geng <i>et al.</i> , 2008)
	0.18% CNTs	PM + HE	682	34.2	(Kondoh <i>et al.</i> , 2009)
	0.24% CNTs		704	38.1	
	0.35% CNTs		754	34.8	
	1% CNTs	SPS + HE	625	–	(Kondoh <i>et al.</i> , 2012)
	2% CNTs		662		
	3% CNTs		853		
	0.2% MWCNTs	SPS	898		(Wang <i>et al.</i> , 2015)
	0.4% MWCNTs		1092		
	0.6% MWCNTs		1052		
	0.8% MWCNTs		1015		
Ti6Al4V	1.0% MWCNTs		853		
	10% TiB	MA + HIP	–	0.25	(Godfrey <i>et al.</i> , 2000)
	20% TiB		1170	2.5	
	20% TiB	MA + HP	1018	0.1	(Gorsse and Miracle, 2003)
	20% TiB	PM + HE	1215	0.5	
	40% TiB		864	0	
	5% TiC	SPS	995	3	(Lagos <i>et al.</i> , 2016)
Ti-24.3Mo	10% TiC		1060	3	
	34% TiB	PM + HP + HT	1105	0.9	(Panda and Ravi, 2003)
Ti-53Nb	34% TiB		724	1.7	
Ti-4.5Al-6.8Mo-1.5Fe	5% TiB	HVC	1038	2.19	(Yan <i>et al.</i> , 2014)
	10% TiB		1147		
	15% TiB		741		
	20% TiB		521		
Ti-6Al-2Zr-1Mo-1V	5% TiC	LMD	925.87	4.32	(Liu <i>et al.</i> , 2009)
	10% TiC		845.27	1.23	
	15% TiC		806.38	1.33	

Note: VAR: Vacuum Arc Remelting; HS: Hot Swaged; SHS: Self-propagating High-Temperature Synthesis; PHIP: Pseudo Hot Isostatic Pressing; MS: Magnetron Sputtering; PM: Powder Metallurgy; RHP: Rapid Hot Pressing; HE: Hot Extrusion; SPS: spark plasma sintering; MA: Mechanical alloying; HT: Heat Treatment; HVC: High-Velocity Compaction; LMD: Laser Melted Deposition.

form of particles, whiskers, or fibers in a ductile Ti matrix can enhance the hardness significantly enhances its hardness and hence the wear resistance of the Ti matrix. Although, fiber-containing titanium composites have rarely been preferred for wear-resistant applications owing to their anisotropic properties and high cost.

Several researchers have studied the sliding wear response of titanium matrix composites (Kim *et al.*, 2011; Zi-Run *et al.*, 2017; Kang *et al.*, 2016; Kim *et al.*, 2013; Singh *et al.*, 2019; Attar *et al.*, 2017). Kim *et al.* (2011) studied the effect of (TiB + TiC) on the wear and friction response of titanium matrix. Further, with the addition of B₄C particles to commercially pure (CP) Ti used vacuum induction melting to synthesize TMMCs. It was They established that the presence of 20% content of the secondary reinforcement is the most preferred way to enhance the wear and friction behavior. It was also concluded that the wear behavior of the Ti matrix improved with the progressive addition of the reinforcement.

An *et al.* (2018) effectively synthesized in-situ TiBw/Ti64 composites using the powder metallurgical process comprising a network structure. It was concluded that the TiBw network structure boundary comprehensively resisted abrasive wear. This was attributed to the network boundary acting as a barrier resulting in improved hardness and sliding wear characteristics of the Ti64 alloy. Further, it was observed that the size of the network closely influenced the wear properties and the mechanism. The friction coefficient and wear loss increased from 0.164 to 0.188 and 4.654 mg to 6.110 mg, respectively, and concluded that the presence of 8.5 vol% TiBw exhibited the highest wear resistance for a network size of 60 μ m. The wear mechanism observed was micro-cutting and brittle debonding with the increment in the size of the network from 60 to 200 μ m, respectively.

Biocompatibility

In recent studies, TMMCs are gaining immense attention as a potential biomaterial especially in the field of orthopedic implants and devices (Comín *et al.*, 2017; Kumar *et al.*, 2013b; Chu *et al.*, 2006; Chen *et al.*, 2017). HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a bioceramic used for hard tissue implants in human applications. Its chemical and crystallographic structure is very comparable to the natural bone (Weiner and Wagner, 1998). The presence of hydroxyapatite (HA) in the titanium matrix has been increasingly studied for biomedical properties to establish its suitability. The Ti-HA composites resulted in a beneficial arrangement of HA for the biocompatibility and strength properties of titanium. Further, HA is bioactive, nontoxic, and biocompatible resulting in higher osseointegration between the bones and the implants (Ong and Chan, 2000). However, a major limitation of using HA on its own is its limited load-bearing capacity. In contrast, Ti has a higher load-bearing capacity, high biocompatibility, and low cytotoxicity. As a result, Ti-HA composites have been believed to have a promising material for orthopedic applications.

The easiest way to synthesize Ti-HA composites is by solid-state processing namely powder metallurgy process (Ning and Zhou, 2008; Comin *et al.*, 2013). Powder metallurgy uses Ti and HA powders to develop high-performance sintered composites wherein the HA particles are uniformly distributed within the Ti matrix. Recently, the FAST (field-assisted sintering technique) has been effectively utilized to synthesize near dense composites at lower energy costs and time frames (Kumar *et al.*, 2013a). Furthermore, studies on synthesizing such composites with biocompatible properties have also been reported using the additive manufacturing process (Qian *et al.*, 2015).

Magnesium Matrix Composites

Magnesium (Mg) is the sixth most abundant element making up $\sim 2.7\%$ by weight of the earth's crust. Mg is the lightest structural element with a density of 1.74 g cm^{-3} is $\sim 35\%$ and $\sim 77\%$ lighter than that of aluminum and steel, respectively (Gupta and Sharon, 2011). In addition to its lightweight, Mg-based materials exhibit enhanced mechanical, thermal, and damping properties, good castability, machinability, and superior resistance to electromagnetic radiation (Itoi *et al.*, 2008; Nguyen *et al.*, 2009; Meenashisundaram and Gupta, 2016). In the past decade, the potential for Mg as a "biomaterial" has encouraged a lot of research with a noticeable increase in the number of scientific publications investigating novel magnesium alloys and composites containing biocompatible reinforcements (Farraro *et al.*, 2014). Mg exhibits superior biocompatibility, shows no indications of local or systemic toxicity (Staiger *et al.*, 2006; Sietsema, 1995; Ramirez and Hurt, 1977), and is the second most abundant intracellular cation being essential for body metabolism (Martin and Preedy, 2014; Xin *et al.*, 2011). With an elastic modulus closer to the natural bone, Mg-based materials when used as an implant material in orthopedic applications can be successful in mitigating stress-shielding effects and possibly eliminate further corrective procedures.

However, the limited ductility of Mg at room temperature and low wet corrosion resistance restricts its usage in many applications. For enhancement of mechanical properties of Mg materials, the addition of inexpensive low volume fraction nanoparticulates (NPs) resulting in dispersion strengthening can be a valid approach when compared to grain refinement achieved by alloying (Umeda *et al.*, 2010). The selection of reinforcements for magnesium composite technology targeting orthopedic applications plays a vital role in the improvement of mechanical properties. Metal oxides (MO) such as Al_2O_3 (Wong *et al.*, 2005), TiO_2 (Meenashisundaram *et al.*, 2015b), Y_2O_3 (Tun and Gupta, 2007), ZrO_2 (Hassan *et al.*, 2013) and ZnO (Tun *et al.*, 2013) have been successfully used as a secondary reinforcement in the Mg matrix owing to their enhanced mechanical and thermal behavior at elevated temperatures. The MO NPs do not undergo further oxidation and are chemically presenting an exciting alternative in the composite technology, not only in the ease of handling and processing but also in improving the properties of the metal matrix. Further, calcium phosphate-based reinforcements have also been viable to improve the overall properties of magnesium (Parande *et al.*, 2018a; Kuśnierczyk and Basista, 2017; Ratna Sunil *et al.*, 2014; He *et al.*, 2011). Some of the interesting results are discussed in this section and presented in Table 3.

Recent developments in magnesium matrix composites

Zhang *et al.* (2014) studied the microstructure and mechanical response of Alumina (Al_2O_3) fibers and particles containing AM60-based hybrid composite. The microstructure studies revealed that both the fibers and particles were uniformly dispersed within the magnesium alloy matrix with limited agglomeration. The elastic modulus, hardness, tensile strengths of the hybrid composites were observed to be higher than that of the AM60 matrix alloy.

In a study, Mg-2 vol% SiO_2 composites displayed excellent refinement in grains with superior mechanical and damping properties (Parande *et al.*, 2016). From the corrosion perspective, the addition of bioglass also improved the mechanical response and biocompatibility and reduced the hydrogen evolution in the composites (Radha and Sreekanth, 2017). These properties of the composites were found to be comparable to the natural bone making them an exciting choice for implant applications (Parande *et al.*, 2016).

Meenashisundaram *et al.* (2015a) used disintegrated melt deposition technique followed by hot extrusion to fabricate Mg- TiO_2 nanocomposites. Mg-1.98 vol% TiO_2 nanocomposite displayed the least grain size. Mg-2.5 vol% TiO_2 nanocomposite displayed an increment in yield strength, ultimate strength, and fracture strain of $\sim 37\%$, $\sim 9\%$, and $\sim 31\%$, respectively in comparison with monolithic magnesium.

Kujur *et al.* (2017) studied the influence of the addition of 0.5, 1.0, and 1.5 vol% of Sm_2O_3 NPs to the microstructural and compression properties of pure Mg. The grain size reduced with the progressive incorporation of Sm_2O_3 NPs to monolithic Mg.

Table 3 Mechanical and corrosion properties of magnesium-matrix composites

Material	Processing technology	UCS (MPa)	UTS (MPa)	TYS (MPa)	Elongation (%)	I_{corr} (A/cm ²)	References
Mg60	As cast	580	–				(Wong <i>et al.</i> , 2017)
Mg67		440					
Mg60T40		800					
Mg67T40		700					
Mg-2Zn-0.5Ca/1 β -TCP	Casting	–				789.9	(Huang <i>et al.</i> , 2015)
β -Ca ₃ (PO ₄) ₂ /Mg-Zn	PM + Extrusion	–		183	–	7	(Yan <i>et al.</i> , 2017)
Mg-Bredigite 40 vol%			190	–			(Dezfuli <i>et al.</i> , 2017)
Mg-0.5SiO ₂		220	–				(Parande <i>et al.</i> , 2016)
Mg-1SiO ₂		203					
Mg-2SiO ₂	PM	207					
Mg-Mn-Zn-Zr		–				1.62×10^{-4}	(Liu <i>et al.</i> , 2017; Kowalski <i>et al.</i> , 2016)
Mg-Mn-Zn-Zr-5HA						3.39×10^{-4}	
Mg-Mn-Zn-Zr-5BG						1.49×10^{-4}	
microcrystalline Mg						3.34×10^{-4}	
Mg-CS 10 wt%		178	–				(Huan <i>et al.</i> , 2016)
Mg-CS 20 wt%		235					
Mg-CS 30 wt%		232					
Mg-CS 40 wt%		212					
Mg-CS 50 wt%		170					
Mg-5HAP	PM + Extrusion	222	–				(Del Campo <i>et al.</i> , 2014)
Mg-10HAP		219					
Mg-15HAP		216					
Mg-0.58(vol%)TiO ₂	DMD	285	128	–	10	–	(Meenashisundaram <i>et al.</i> , 2015a)
Mg-0.97(vol%)TiO ₂		278.4	154		10.8		
Mg-1.98(vol%)TiO ₂		297	165		11.5		
Mg-2.5(vol%)TiO ₂		305.5	170		10		
AZ91–10FA	PM	–			5.78	7.4×10^{-5}	(Razavi <i>et al.</i> , 2010)
AZ91–20FA					5.32	2.3×10^{-6}	
AZ91–30FA					4.51	3.5×10^{-7}	

Mg-1.5 vol% Sm₂O₃ displayed the highest reduction of 46.7% in grain size as compared to pure Mg. NPs are fairly distributed in the magnesium matrix as shown in Fig. 10. Near uniform dispersion of secondary particles in the magnesium matrix is important for realizing Orowan strengthening leading to enhanced strength properties (Parande *et al.*, 2018b; Malaki *et al.*, 2019; Parande *et al.*, 2020; Gupta and Wong, 2015; Kumar Meenashisundaram *et al.*, 2017). Mg-1.5 vol% Sm₂O₃ nanocomposite showed the highest increase in the yield strength and ultimate strength of ~56% and 53% as compared to monolithic Mg. The fracture strain of Mg-Sm₂O₃ nanocomposites was similar to or higher than pure Mg.

Gu *et al.* (2010) used powder metallurgy process to develop Mg/(10, 20, and 30 wt%) HAP composite and studied the effect of HAP on the microstructure, corrosion, cytotoxicity, and mechanical properties. HAP particulates were observed to be agglomerated in the Mg matrix at regular intervals for the Mg/20 wt% HAP composite. The overall properties were observed to reduce with the presence of HAP for all the composites.

Chen *et al.* (2016) studied the strength properties of the AZ91, porous HAP, and AZ91/HAP composite. It was observed that AZ91 displays higher strength and fracture strain values as compared with the HAP and HAP containing AZ91 composite. Although, porous HAP displays lower strength and ductility values as compared to AZ91 and HAP containing AZ91 composite. The presence of HAP particles greater than 10 wt% resulted in the decrement of yield strength and ultimate strength, under tensile mode. This was owing to the high amount of clustering of HAP particles resulting in the formation of defects and pores at the matrix level (Hassan and Gupta, 2005).

Khanra *et al.* (2010) compared the effect of chemically sterilized HAP powder (0, 5, 10, and 15 wt%) HAP on Mg and ZM61 alloy synthesized using the extrusion process. The grain size with the presence of HAP decreased for both Mg and ZM61 alloy. The tensile strength of the composites decreased with the progressive addition of HAP. Further, the compressive strength of the composites increased and the ductility of the composites decreased with the presence of HAP. Xu *et al.* (2009) studied that the Mg–15% HAP composites displayed superior yield and ultimate strengths in compressive modes but a decreased tensile strength properties due to the increased addition of HAP.

Parande *et al.* (2018a) studied the effect of the addition of (0.5, 1, and 1.5) vol% β -tricalcium phosphate (β -TCP) on the microstructure, damping, and immersion characteristics of monolithic Mg. The presence of β -TCP improved the yield strength, ultimate strength, and fracture strain under compressive mode by about ~34%, ~53%, and ~22%, respectively, in comparison

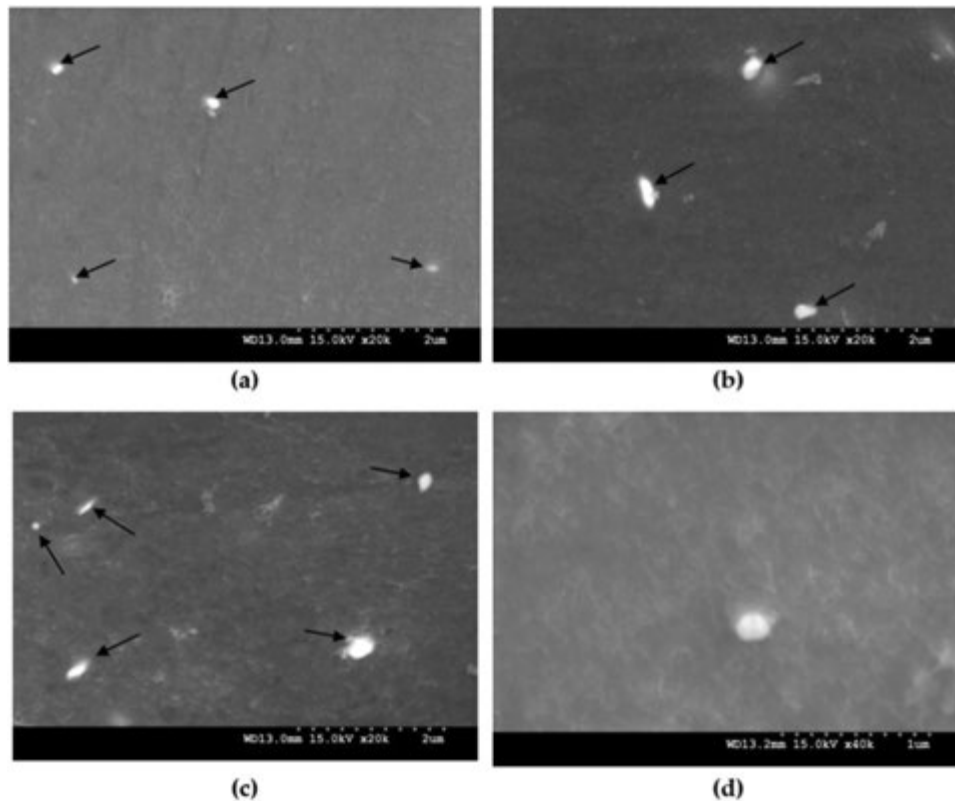


Fig. 10 Scanning electron microscopy (SEM) images showing the distribution of Sm_2O_3 nanoparticles (indicated by the arrows) in Mg- Sm_2O_3 nanocomposites: (a) Mg-0.5 vol% Sm_2O_3 (b) Mg-1 vol% Sm_2O_3 (c) Mg-1.5 vol% Sm_2O_3 (d) interfacial integrity of Mg-1.0 vol% Sm_2O_3 nanocomposite. Reproduced from Kujur, M.S., Mallick, A., Manakari, V., *et al.*, 2017. Significantly Enhancing the Ignition/Compression/Damping Response of Monolithic Magnesium by Addition of Sm2O3 Nanoparticles. *Metals* 7 (9), 357.

with pure Mg. Mg-1.5 vol% β -TCP composite showed a superior $\sim 70\%$ grain refinement when compared to pure Mg (Fig. 11). Refined grain size is vital in improving the yield strength of magnesium composites by activating Hall-Petch strengthening (Parande *et al.*, 2020; Yan *et al.*, 2017; Parande *et al.*, 2018c).

Parande *et al.* (2019) reinforced low cost (3, 5, and 7 wt%) eggshell (ES) particles to develop Mg-2.5 wt% Zn composites synthesized using an energy-efficient DMD process. The presence of 3, 5, and 7 wt% ES displayed a compressive yield strength (0.2CYS) to be ~ 113 MPa, ~ 116 MPa, and ~ 117 MPa, respectively, which is $\sim 3.6\%$, $\sim 6.4\%$, and $\sim 7.3\%$ as compared to that of the Mg-2.5Zn alloy (~ 109 MPa). Mg-2.5Zn-3ES and Mg-2.5Zn-5ES composites showed a fracture strain value of $\sim 30\%$ and $\sim 34\%$, respectively. This is a $\sim 14.5\%$ and $\sim 29.7\%$, respectively enhancement compared to the Mg-2.5Zn alloy.

Mg-40 vol% bredigite composites synthesized using the powder metallurgy process displayed strength properties similar to that of natural bone. The degradation of Mg was decreased 24 times with the presence of bredigite particles in the Mg matrix (Dezfuli *et al.*, 2017). Mg60Zn35Ca5BMGC containing 40 vol% of Ti particles displayed a near-uniform lower rate of degradation when compared to other composite formulations. Mg60Zn35Ca5BMGC experiences slower anodic dissolution of Mg^{2+} and hence the corrosion protection is observed to better with the presence of the reinforcement (Wong *et al.*, 2017).

Mg-matrix bio-nano composite containing HAP, MgTiO_3 , $\text{Mg}_3(\text{PO}_4)_2$, and $\text{Mg}(\text{OH})_2$ phases was studied (Khalajabadi *et al.*, 2015). It was observed that the increased milling times and HAP amounts resulted in a lower corrosion rate in the SBF solution revealed.

The effect of reinforcing various amounts of Fluorapatite (FA) nanoparticles (10, 20, 30 wt%) on corrosion and mechanical response of AZ91 alloy was studied (Razavi *et al.*, 2010). The corrosion properties were improved with the presence of FA and a progressive increase in FA improved the corrosion resistance further. Formation of a protective hydroxide layer on the surface of the composite thereby facilitating surface protection and potential for bone remodeling (Yan *et al.*, 2017). A reduction in the deformability of the AZ91 alloy was observed with the increased presence of FA reinforcements. The presence of hard FA ceramics was observed to increase the hardness behavior of AZ91 alloy. This was owing to the presence of FA particles at the matrix interface thereby obstructing the deformation locally during the indentation. The improvement in corrosion resistance was observed with the increase in the amount of FA in AZ91 alloy (Razavi *et al.*, 2010).

In a study, Cao *et al.* (2017) used spark plasma sintering to synthesize in-situ Mg composites from Mg and ZnO powder. The corrosion properties were evaluated using immersion and electrochemical tests in the HBSS solution. Mg/10 wt% ZnO composite revealed an improvement in the corrosion resistance compared with the other formulations. Fig. 12 revealed the SEM of post

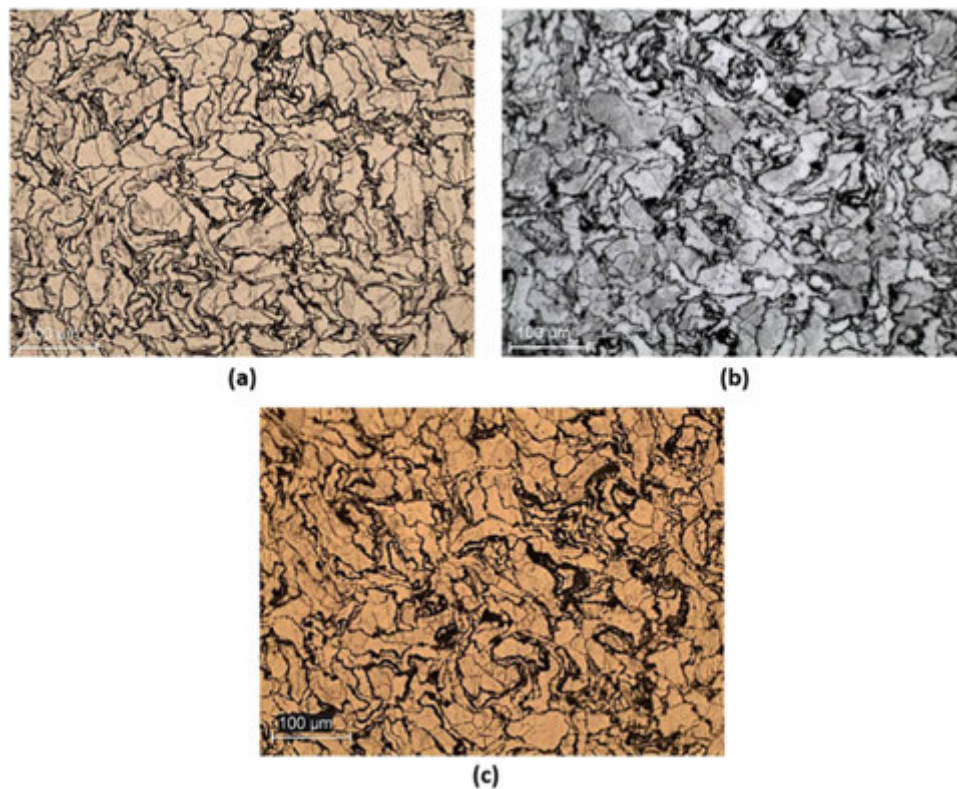


Fig. 11 Optical micrography images of Mg- β -TCP composites: (a) Mg-0.5 TCP; (b) Mg-1.0 TCP; and, (c) Mg-1.5 TCP. Reproduced from Parande, G., Manakari, V., Gupta, H., Gupta, M., 2018a. Magnesium- β -tricalcium phosphate composites as a potential orthopedic implant: A mechanical/damping/immersion perspective. *Metals* 8 (5), 343.

immersed Mg-ZnO samples. The observations revealed the calcium phosphate layer formation on the surface of the sample. This formation of the protective phosphate layer is known to have a pronounced effect on the osseointegration of the materials and hence can be a promising candidate for implant applications.

Shuai *et al.* (2020) studied the effect of MgO-coated reduced graphene oxide (RGO) containing AZ61 alloy synthesized using selective laser melting (SLM) process. The presence of MgO coated RGO improved the mechanical and corrosion behavior of AZ61 alloy when compared to only RGO addition to AZ61 alloy. Also, the progressive addition of the RGO/MgO content refined the grain size significantly. The grain size refinement due to the presence of reinforcement resulting in an improved hardness value from 90 ± 2 – 115 ± 2 HV with the progressive addition from 0 wt% to 4 wt%. AZ61-3 wt% RGO/MgO revealed the highest compressive strength of 221 ± 2 MPa which was 30% higher than the base matrix. This was attributed to the superior interfacial integrity between the magnesium matrix and the RGO/MgO reinforcement. The corrosion behavior of AZ61-3 wt% RGO/MgO composite exhibited the lowest corrosion rate of 1.05 mm/y.

Shahin *et al.* (2020) studied the effect of GNP on the microstructural and mechanical behavior of sintered Mg-Zr alloy. A near homogenous distribution of GNP was observed in the Mg-Zr alloy which was attributed to the optimized parameters used during high energy ball milling. The ultimate compressive strength was increased by $\sim 91\%$ with respect to pure Mg owing to the solid solution strengthening effect between the Mg, Zr, and GNP phases. The corrosion rate was decreased with the presence of GNP from 5.5 to 3 mm/y owing to the near-uniform presence of GNP and the refinement in grain size.

Saberi *et al.* (2020) studied the effect of xGNP ($x = 0, 0.5, 1.0$, and 2.0 wt%) graphene nanoparticles on the mechanical, corrosion and biological responses of Mg-3 wt% Zn-1 wt% Ca alloy synthesized using the semi-powder metallurgy process. The study revealed that 1 wt% of GNP addition observably enhanced the compressive strength. This was attributed to the refinement in grain size and superior interfacial integrity between the alloy matrix and the GNP reinforcement. However, the presence of 2 wt% GNP in the Mg matrix exhibited limited clustering in the matrix and reduced the interfacial bonding leading to a reduction in the strength properties. Electrochemical corrosion tests were performed and the Mg-3Zn-1Ca/1 wt% GNP composite showed the lowest corrosion current density ($112.89 \mu\text{A}/\text{cm}^2$). This was attributed to the pore filling on the surface of the composite. However, Mg-3Zn-1Ca/2 wt% GNP displayed a high corrosion current density ($420.76 \mu\text{A}/\text{cm}^2$) as compared to 1 wt%. Microgalvanic corrosion between Mg and GNP was attributed to this increase in corrosion density owing to the presence of matrix voids and cracks.

Parande *et al.* (2018a) studied the immersion response of Mg-TCP composites in HBSS. The presence of TCP significantly decreased the corrosion rate. All the TCP composites also displayed a near-uniform corrosion rate with the increase in immersion

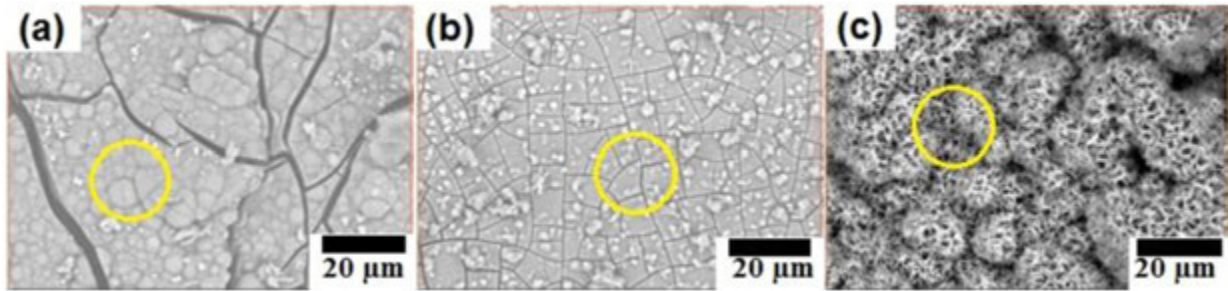


Fig. 12 SEM observation of immersed Mg-ZnO samples in HBSS. Reproduced from Cao, N.Q., Pham, D.N., Kai, N., *et al.*, 2017. In vitro corrosion properties of Mg matrix in situ composites fabricated by spark plasma sintering. *Metals* 7 (9), 358.

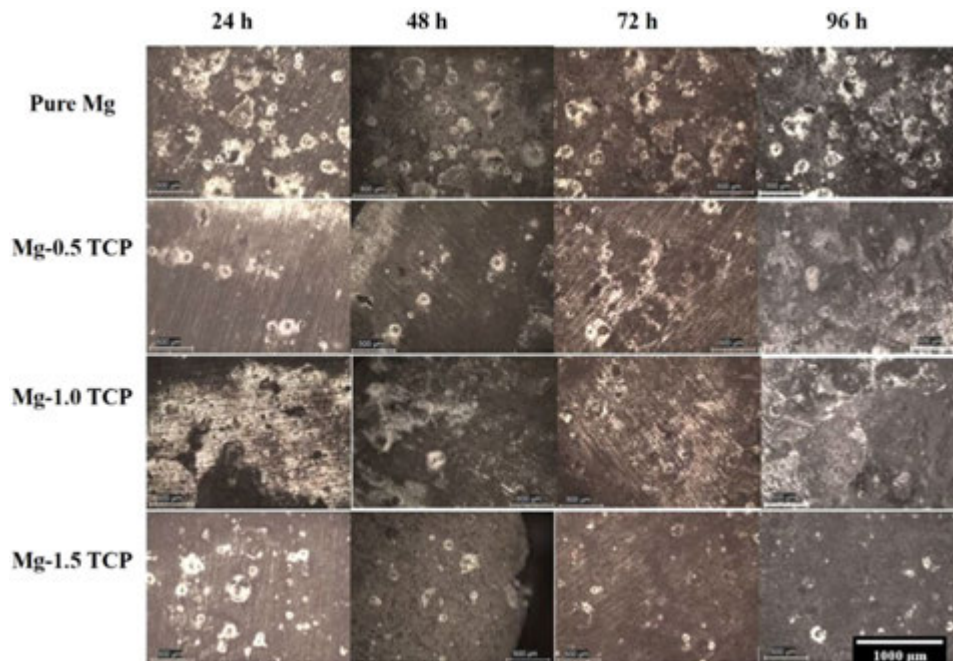


Fig. 13 Optical micrographs of pure magnesium and Mg (0.5, 1.0, and 1.5) vol% β -TCP composites after 24, 48, 72, and 96 h of immersion. Reproduced from Parande, G., Manakari, V., Gupta, H., Gupta, M., 2018a. Magnesium- β -tricalcium phosphate composites as a potential orthopedic implant: A mechanical/damping/immersion perspective. *Metals* 8 (5), 343.

time. **Fig. 13** shows the optical micrographs of the samples under immersion. The pit formation post corrosion was evident in pure Mg and the TCP composites showed a lower prevalence of corroded pits. The SEM analysis of the corroded surface of the Mg-1.0 TCP composite samples post 96 h of immersion is shown in **Fig. 14** leading to severe cracking on the sample surface with two types of layers namely quasi-adherent layer and cracked layer being formed. Several uneven pits post corrosion with uneven sizes and microcracks were observed throughout the monolithic and composite samples.

Summary

The article discusses the recent trends in the field of eco-friendly metal matrix composites and briefly summarises the processing technologies and properties of the composites. The following observations have been drawn from this attempt.

- The metal matrix composite community has made significant strides in utilizing low cost inexpensive secondary reinforcements to replace high-density toxic metals to develop materials with holistic importance.
- In the case of zinc-based composites, several articles have been published on the influence of secondary reinforcements in various morphologies on the response of ZA27 alloy synthesized using various methodologies. Natural fillers, industrial wastes amongst others have been successfully used to develop high-performance zinc matrix composites. Going forward, it would be

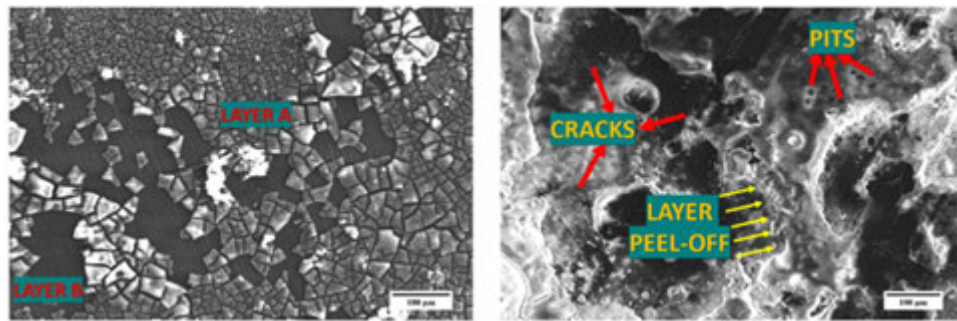


Fig. 14 Scanning Electron Microscope (SEM) analysis of Mg-1.0 TCP composite post 96 h of Hanks balanced salt solution (HBSS) immersion. Reproduced from Parande, G., Manakari, V., Gupta, H., Gupta, M., 2018a. Magnesium- β -tricalcium phosphate composites as a potential orthopedic implant: A mechanical/damping/immersion perspective. *Metals* 8 (5), 343.

advisable to explore different options to alloy zinc to decrease the amount of aluminum in the alloy in the overall interest of recyclability and non-toxicity.

- In the case of titanium-based composites, additive manufacturing technologies have been used to a successful extent in the past decade. Using these processes to form near net-shaped products for aerospace industries and custom products for orthopedic implant sectors can gain higher acceptance. The influence of natural fillers like rice husk, eggshell, and industrial wastes like fly ash can be further explored. Replacing aluminum and rare earth elements with Nb, Zr, Si, Zn amongst others can be explored to improve the functional properties of the titanium matrix.
- In the case of magnesium matrix composites, the concept of Eco-Mg-based alloys has made a significant contribution to the knowledge of the design and development of low-cost high-performance magnesium materials. This approach can yield favorable results in weight critical applications in the transportation sectors and fracture fixation procedures in biomedical sectors. The possibility of producing these novel composites using additive manufacturing techniques can be explored in the future.

References

- Ajayan, P.M., Ebbesen, T.W., Ichihashi, T., *et al.*, 1993. Opening carbon nanotubes with oxygen and implications for filling. *Nature* 362 (6420), 522–525.
- Alaneme, K., Fatile, B., Borode, J., 2014. Mechanical and corrosion behaviour of Zn-27Al based composites reinforced with groundnut shell ash and silicon carbide. *Tribology in Industry* 36 (2).
- Alaneme, K.K., Ajayi, O.J., 2017. Microstructure and mechanical behavior of stir-cast Zn-27Al based composites reinforced with rice husk ash, silicon carbide, and graphite. *Journal of King Saud University – Engineering Sciences* 29 (2), 172–177.
- Alaneme, K.K., Adeoye, K.O., Oke, S.R., 2016. Mechanical and wear behaviour of steel chips reinforced Zn27Al composites. *Leonardo Electronic Journal of Practices and Technologies* 29, 1–16.
- Alaneme, K.K., Akintunde, I.B., Olubambi, P.A., Adewale, T.M., 2013. Fabrication characteristics and mechanical behaviour of rice husk ash – Alumina reinforced Al-Mg-Si alloy matrix hybrid composites. *Journal of Materials Research and Technology* 2 (1), 60–67.
- Almomani, M., Hayajneh, M.T., Draidi, M., 2017. Corrosion investigation of zinc – aluminum alloy matrix (ZA-27) reinforced with alumina (Al_2O_3) and fly ash. *Particulate Science and Technology* 35 (4), 439–447.
- An, Q., Huang, L.J., Bao, Y., *et al.*, 2018. Dry sliding wear characteristics of in-situ TiBw/Ti₆Al₄V composites with different network parameters. *Tribology International* 121, 252–259.
- Anderson, R.E., 1998. Titanium matrix composite turbine engine component consortium (TMCTECC). In: *Advanced Materials and Process Technology Information Analysis Center (AMPTIAC) Newsletter*, Winter.
- Attar, H., Ehtemam-Haghighi, S., Kent, D., *et al.*, 2017. Nanoindentation and wear properties of Ti and Ti-TiB composite materials produced by selective laser melting. *Materials Science and Engineering: A* 688, 20–26.
- Avedesian, M.M., Baker, H., 1999. *ASM Specialty Handbook: Magnesium and Magnesium Alloys*. ASM international.
- Barnhurst, R., Beliste, S., 1992. *Corrosion properties of Zamak and ZA alloys*. Quebec: Noranda Technology Centre.
- Bettge, D., Günther, B., Wedell, W., *et al.*, 2007. Mechanical behavior and fatigue damage of a titanium matrix composite reinforced with continuous SiC fibers. *Materials Science and Engineering: A* 452–453, 536–544.
- BhaskarRaju, S., Hemanth, K., Jayasimha, S., 2017. Mechanical characterization of ZA-27 reinforced with SiCp MMCs. In: *Proc Of IntConf on Current Trends in Eng Sci and Tech*, pp. 228–232.
- Cao, N.Q., Pham, D.N., Kai, N., *et al.*, 2017. In vitro corrosion properties of Mg matrix in situ composites fabricated by spark plasma sintering. *Metals* 7 (9), 358.
- Chaudhari, R., Bauri, R., 2018. A novel functionally gradient Ti/TiB/TiC hybrid composite with wear resistant surface layer. *Journal of Alloys and Compounds* 744, 438–444.
- Chen, B., Yin, K.-Y., Lu, T.-F., *et al.*, 2016. AZ91 magnesium alloy/porous hydroxyapatite composite for potential application in bone repair. *Journal of Materials Science & Technology* 32 (9), 858–864.
- Chen, Y., Zhang, J., Dai, N., *et al.*, 2017. Corrosion behaviour of selective laser melted Ti-TiB biocomposite in simulated body fluid. *Electrochimica Acta* 232, 89–97.
- Choi, B.-J., Kim, Y.-J., 2013. In-situ (TiB + TiC) particulate reinforced titanium matrix composites: Effect of B 4C size and content. *Metals and Materials International* 19 (6), 1301–1307.
- Chu, C., Xue, X., Zhu, J., Yin, Z., 2006. In vivo study on biocompatibility and bonding strength of Ti/Ti-20vol% HA/Ti-40vol% HA functionally graded biomaterial with bone tissues in the rabbit. *Materials Science and Engineering: A* 429 (1), 18–24.
- Comin, R., Reyna, L.A., Cid, M.P., Oldani, C.R., Salvatierra, N.A., 2013. Cytotoxicity of hydroxyapatite and morphology in composites with Ti. *IEEE Latin America Transactions* 11 (1), 97–100.

- Comín, R., Cid, M.P., Grinschpun, L., Oldani, C., Salvatierra, N.A., 2017. Titanium-hydroxyapatite composites sintered at low temperature for tissue engineering: In vitro cell support and biocompatibility. *Journal of Applied Biomaterials & Functional Materials* 15 (2), 176–183.
- Cui, S., Cui, C., Xie, J., Liu, S., Shi, J., 2018. Carbon fibers coated with graphene reinforced TiAl alloy composite with high strength and toughness. *Scientific Reports* 8 (1), 1–8.
- Dalmis, R., Cuvalci, H., Canakci, A., Guler, O., 2016. Investigation of graphite nano particle addition on the physical and mechanical properties of Za27 composites. *Advanced Composites Letters* 25 (2), (096369351602500202).
- Del Campo, R., Savoini, B., Muñoz, A., Monge, M., Garcés, G., 2014. Mechanical properties and corrosion behavior of Mg–HAP composites. *Journal of the Mechanical Behavior of Biomedical Materials* 39, 238–246.
- Dezfuli, S.N., Huan, Z., Mol, A., *et al.*, 2017. Advanced bredigite-containing magnesium-matrix composites for biodegradable bone implant applications. *Materials Science and Engineering: C* 79, 647–660.
- Dougherty, T., Xu, Y., Hanizan, A., 2016. Mechanical Properties and Microstructure of PM Ti-Si 3 N 4 Discontinuous Fibre Composite, TMS 2016 145th Annual Meeting & Exhibition. Springer. pp. 721–728.
- Duan, J., 2016. Development of a Numerical Optimization Methodology for the Aluminum Alloy Wheel Casting Process. University of British Columbia.
- Farraro, K.F., Kim, K.E., Woo, S.L., Flowers, J.R., McCullough, M.B., 2014. Revolutionizing orthopaedic biomaterials: The potential of biodegradable and bioresorbable magnesium-based materials for functional tissue engineering. *Journal of Biomechanics* 47 (9), 1979–1986.
- Fatile, O.B., Idu, F.U., Sanya, O.T., 2015. Fabrication characteristics and mechanical behavior of fly ash-alumina reinforced Zn-27Al alloy matrix hybrid composite using stir-casting technique. *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering* 9 (10), 1037–1104.
- Folorunso, D.O., Owoeye, S.S., 2019. Influence of quarry dust-silicon carbide weight percentage on the mechanical properties and tribological behavior of stir cast ZA-27 alloy based hybrid composites. *Journal of King Saud University-Engineering Sciences* 31 (3), 280–285.
- Geng, K., Lu, W., Qin, Y., Zhang, D., 2004. In situ preparation of titanium matrix composites reinforced with TiB whiskers and Y_2O_3 particles. *Materials Research Bulletin* 39 (6), 873–879.
- Geng, L., Ni, D., Zhang, J., Zheng, Z., 2008. Hybrid effect of TiBw and TiCp on tensile properties of in situ titanium matrix composites. *Journal of Alloys and Compounds* 463 (1–2), 488–492.
- Godfrey, T.M.T., Wisbey, A., Goodwin, P.S., Bagnall, K., Ward-Close, C.M., 2000. Microstructure and tensile properties of mechanically alloyed Ti–6Al–4V with boron additions. *Materials Science and Engineering: A* 282 (1), 240–250.
- Gorsse, S., Miracle, D.B., 2003. Mechanical properties of Ti-6Al-4V/TiB composites with randomly oriented and aligned TiB reinforcements. *Acta Materialia* 51 (9), 2427–2442.
- Gu, X., Zhou, W., Zheng, Y., *et al.*, 2010. Microstructure, mechanical property, bio-corrosion and cytotoxicity evaluations of Mg/HA composites. *Materials Science and Engineering: C* 30 (6), 827–832.
- Gupta, M., Leong, E.W.W., 2008. *Microwaves and Metals*. John Wiley & Sons.
- Gupta, M., Ling, S.N.M., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites*. John Wiley & Sons.
- Gupta, M., Sharon, N.M.L., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites*. John Wiley & Sons.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.
- Gupta, M., Gupta, N., 2017. Utilizing magnesium based materials to reduce green house gas emissions in aerospace sector. *Aeronautics and Aerospace Open Access Journal* 1 (1), 1–6.
- Hassan, S., Gupta, M., 2005. Development of high performance magnesium nano-composites using nano- Al_2O_3 as reinforcement. *Materials Science and Engineering: A* 392 (1–2), 163–168.
- Hassan, S.F., Tan, M.J., Gupta, M., 2013. Development of nano-ZrO₂ reinforced magnesium nanocomposites with significantly improved ductility. *Materials Science and Technology* 23 (11), 1309–1312.
- Hayat, M.D., Singh, H., He, Z., Cao, P., 2019. Titanium metal matrix composites: An overview. *Composites Part A: Applied Science and Manufacturing* 121, 418–438.
- He, S.-y., Sun, Y., Chen, M.-f., Liu, D.-b., Ye, X.-y., 2011. Microstructure and properties of biodegradable β -TCP reinforced Mg-Zn-Zr composites. *Transactions of Nonferrous Metals Society of China* 21 (4), 814–819.
- Huan, Z., Xu, C., Ma, B., Zhou, J., Chang, J., 2016. Substantial enhancement of corrosion resistance and bioactivity of magnesium by incorporating calcium silicate particles. *RSC Advances* 6 (53), 47897–47906.
- Huang, Y., Liu, D., Anguilano, L., You, C., Chen, M., 2015. Fabrication and characterization of a biodegradable Mg–2Zn–0.5 Ca/1 β -TCP composite. *Materials Science and Engineering: C* 54, 120–132.
- Itoi, T., Takahashi, K., Moriyama, H., Hirohashi, M., 2008. A high-strength Mg–Ni–Y alloy sheet with a long-period ordered phase prepared by hot-rolling. *Scripta Materialia* 59 (10), 1155–1158.
- Jiang, J., Xiao, G., Che, C., Wang, Y., 2018. Microstructure, mechanical properties and wear behavior of the rheoformed 2024 Aluminum matrix composite component reinforced by Al_2O_3 nanoparticles. *Metals* 8 (6), 460.
- Kang, N., Coddet, P., Liu, Q., Liao, H., Coddet, C., 2016. In-situ TiB/near α Ti matrix composites manufactured by selective laser melting. *Additive Manufacturing* 11, 1–6.
- Kelly, A., 2006. Composite materials after seventy years. *Journal of Materials Science* 41 (3), 905–912.
- Kerns, J., 2016. Powder-metallurgy processes. *Machine design*, pp. 1–5.
- Khalajabadi, S.Z., Kadir, M.R.A., Izman, S., Kasiri-Asgarani, M., 2015. Microstructural characterization, biocorrosion evaluation and mechanical properties of nanostructured ZnO and Si/ZnO coated Mg/HA/TiO₂/MgO nanocomposites. *Surface and Coatings Technology* 277, 30–43.
- Khanra, A.K., Jung, H.C., Yu, S.H., Hong, K.S., Shin, K.S., 2010. Microstructure and mechanical properties of Mg–HAP composites. *Bulletin of Materials Science* 33 (1), 43–47.
- Kim, I., Choi, B., Kim, Y., Lee, Y., 2011. Friction and wear behavior of titanium matrix (TiB + TiC) composites. *Wear* 271 (9–10), 1962–1965.
- Kim, J.-S., Lee, K.-M., Cho, D.-H., Lee, Y.-Z., 2013. Fretting wear characteristics of titanium matrix composites reinforced by titanium boride and titanium carbide particulates. *Wear* 301 (1), 562–568.
- Kiran, T., Kumar, M.P., Basavarajappa, S., Vishwanatha, B., 2013. Mechanical properties of as-cast za-27/gr/sicp hybrid composite for the application of journal bearing. *Journal of Engineering Science and Technology* 8 (5), 557–565.
- Klasik, A., Pietrzak, K., Makowska, K., *et al.*, 2016. Wear resistance of aluminum matrix composites reinforced with Al_2O_3 particles after multiple remelting. *Journal of Materials Engineering and Performance* 25 (8), 3084–3090.
- Kondoh, K., Threrujirapong, T., Umeda, J., Fugetsu, B., 2012. High-temperature properties of extruded titanium composites fabricated from carbon nanotubes coated titanium powder by spark plasma sintering and hot extrusion. *Composites Science and Technology* 72 (11), 1291–1297.
- Kondoh, K., Threrujirapong, T., Imai, H., Umeda, J., Fugetsu, B., 2009. Characteristics of powder metallurgy pure titanium matrix composite reinforced with multi-wall carbon nanotubes. *Composites Science and Technology* 69 (7), 1077–1081.
- Kowalski, K., Nowak, M., Jurczyk, M., 2016. Mechanical and corrosion properties of magnesium-bioceramic nanocomposites. *Archives of Metallurgy and Materials* 61.
- Kubásek, J., Dvorský, D., Čapek, J., Pinc, J., Vojtěch, D., 2019. Zn-Mg biodegradable composite: Novel material with tailored mechanical and corrosion properties. *Materials* 12 (23), 3930.
- Kujur, M.S., Mallick, A., Manakari, V., *et al.*, 2017. Significantly enhancing the ignition/compression/damping response of monolithic magnesium by addition of Sm_2O_3 nanoparticles. *Metals* 7 (9), 357.
- Kumar, A., Biswas, K., Basu, B., 2013a. On the toughness enhancement in hydroxyapatite-based composites. *Acta Materialia* 61 (14), 5198–5215.

- Kumar, A., Webster, T.J., Biswas, K., Basu, B., 2013b. Flow cytometry analysis of human fetal osteoblast fate processes on spark plasma sintered hydroxyapatite-titanium biocomposites. *Journal of Biomedical Materials Research. Part A* 101 (10), 2925–2938.
- Kumar Meenashisundaram, G., Hou Damien Ong, T., Parande, G., *et al.*, 2017. Using lanthanum to enhance the overall ignition, hardness, tensile and compressive strengths of Mg-0.5Zr alloy. *Journal of Rare Earths* 35 (7), 723–732.
- Kuśnierczyk, K., Basista, M., 2017. Recent advances in research on magnesium alloys and magnesium–calcium phosphate composites as biodegradable implant materials. *Journal of Biomaterials Applications* 31 (6), 878–900.
- Kuzumaki, T., Ujiie, O., Ichinose, H., Ito, K., 2000. Mechanical characteristics and preparation of carbon nanotube fiber-reinforced Ti composite. *Advanced Engineering Materials* 2 (7), 416–418.
- Lagos, M.A., Agote, I., Atxaga, G., Adarraga, O., Pambaguian, L., 2016. Fabrication and characterisation of titanium matrix composites obtained using a combination of self propagating high temperature synthesis and spark plasma sintering. *Materials Science and Engineering: A* 655, 44–49.
- Leucht, R., Dudek, H., 1994. Properties of SiC-fibre reinforced titanium alloys processed by fibre coating and hot isostatic pressing. *Materials Science and Engineering: A* 188 (1–2), 201–210.
- Leyens, C., Hausmann, J., Kumpfert, J., 2003. Continuous fiber reinforced titanium matrix composites: Fabrication, properties, and applications. *Advanced Engineering Materials* 5 (6), 399–410.
- Li, S., Sun, B., Imai, H., Mimoto, T., Kondoh, K., 2013. Powder metallurgy titanium metal matrix composites reinforced with carbon nanotubes and graphite. *Composites Part A: Applied Science and Manufacturing* 48, 57–66.
- Li, Z., 2014. Fabrication of in situ TiB₂ particulates reinforced zinc alloy matrix composite. *Materials Letters* 121, 1–4.
- Liu, C., Huang, L., Geng, L., Jiao, Y., Tang, A., 2015. In situ synthesis of (TiC + Ti₃SiC₂ + Ti₅Si₃)/Ti₆Al₄V composites with tailored two-scale architecture. *Advanced Engineering Materials* 17 (7), 933–941.
- Liu, D., Zhang, S.Q., Li, A., Wang, H.M., 2009. Microstructure and tensile properties of laser melting deposited TiC/TiAl₃ titanium matrix composites. *Journal of Alloys and Compounds* 485 (1), 156–162.
- Liu, D., Liu, Y., Zhao, Y., Huang, Y., Chen, M., 2017. The hot deformation behavior and microstructure evolution of HA/Mg-3Zn-0.8Zr composites for biomedical application. *Materials Science and Engineering C: Materials for Biological Applications* 77, 690–697.
- Lobley, C., Guo, X., 1999. Viable routes to large-scale commercialisation of silicon carbide fibre titanium matrix composites. *Materials Technology* 14 (3), 133–138.
- MacKay, R., Brindley, P., Froes, F., 1991. Continuous fiber-reinforced titanium aluminide composites. *JOM* 43 (5), 23–29.
- Madakson, P., Yawas, D., Apasi, A., 2012. Characterization of coconut shell ash for potential utilization in metal matrix composites for automotive applications. *International Journal of Engineering Science and Technology* 4 (3), 1190–1198.
- Malaki, M., Xu, W., Kasar, A.K., *et al.*, 2019. Advanced Metal Matrix Nanocomposites. *Metals* 9 (3), 330.
- Martin, C.R., Preedy, V.R., 2014. *Diet and Nutrition in Dementia and Cognitive Decline*. Academic Press.
- Meenashisundaram, G., Nai, M., Gupta, M., 2015b. Effects of primary processing techniques and significance of hall-petch strengthening on the mechanical response of magnesium matrix composites containing TiO₂ nanoparticulates. *Nanomaterials* 5 (3), 1256–1283.
- Meenashisundaram, G.K., Gupta, M., 2016. Emerging environment friendly, magnesium-based composite technology for present and future generations. *JOM* 68 (7), 1890–1901.
- Meenashisundaram, G.K., Nai, M.H., Almajid, A., Gupta, M., 2015a. Development of high performance Mg–TiO₂ nanocomposites targeting for biomedical/structural applications. *Materials & Design* (1980–2015) 65, 104–114.
- Miloradovic, N., Stojanovic, B., 2013. Tribological behaviour of ZA27/10SiC/1Gr hybrid composite. *Journal of the Balkan Tribological Association* 19 (1), 97–105.
- Morsi, K., Patel, V., 2007. Processing and properties of titanium–titanium boride (TiB w) matrix composites – A review. *Journal of Materials Science* 42 (6), 2037–2047.
- Munir, K.S., Kingshott, P., Wen, C., 2015. Carbon nanotube reinforced titanium metal matrix composites prepared by powder metallurgy – A review. *Critical Reviews in Solid State and Materials Sciences* 40 (1), 38–55.
- Nguyen, Q.B., Gupta, M., Srivatsan, T.S., 2009. On the role of nano-alumina particulate reinforcements in enhancing the oxidation resistance of magnesium alloy AZ31B. *Materials Science and Engineering: A* 500 (1–2), 233–237.
- Ning, C., Zhou, Y., 2008. Correlations between the in vitro and in vivo bioactivity of the Ti/HA composites fabricated by a powder metallurgy method. *Acta Biomaterialia* 4 (6), 1944–1952.
- Ong, J.L., Chan, D.C., 2000. Hydroxyapatite and their use as coatings in dental implants: A review. *Critical Reviews in Biomedical Engineering* 28 (5–6), 667–707.
- Owoeye, S.S., Folorunso, D.O., Oji, B., Borisade, S.G., 2019. Zinc-aluminum (ZA-27)-based metal matrix composites: A review article of synthesis, reinforcement, microstructural, mechanical, and corrosion characteristics. *The International Journal of Advanced Manufacturing Technology* 100 (1–4), 373–380.
- Panda, K.B., Ravi Chandran, K.S., 2003. Synthesis of ductile titanium–titanium boride (Ti–TiB) composites with a beta-titanium matrix: the nature of TiB formation and composite properties. *Metallurgical and Materials Transactions A* 34 (6), 1371–1385.
- Pank, D., Jackson, J., 1993. Metal-matrix composite processing technologies for aircraft engine applications. *Journal of Materials Engineering and Performance* 2 (3), 341–346.
- Parande, G., Manakari, V., Meenashisundaram, G.K., Gupta, M., 2016. Enhancing the hardness/compression/damping response of magnesium by reinforcing with biocompatible silica nanoparticulates. *International Journal of Materials Research* 107 (12), 1091–1099.
- Parande, G., Manakari, V., Gupta, H., Gupta, M., 2018a. Magnesium-β-tricalcium phosphate composites as a potential orthopedic implant: A mechanical/damping/immersion perspective. *Metals* 8 (5), 343.
- Parande, G., Manakari, V., Koppa, S.D.S., Gupta, M., 2018b. Utilizing low-cost eggshell particles to enhance the mechanical response of Mg-2.5Zn magnesium alloy matrix. *Advanced Engineering Materials* 20 (5), 1700919.
- Parande, G., Manakari, V., Sharma Koppa, S.D., Gupta, M., 2019. A study on the effect of low-cost eggshell reinforcement on the immersion, damping and mechanical properties of magnesium–zinc alloy. *Composites Part B: Engineering* 182, 107650.
- Parande, G., Manakari, V., Wakeel, S., Kujur, M.S., Gupta, M., 2018c. Enhancing mechanical response of monolithic magnesium using nano-NiTi (Nitinol) particles. *Metals* 8 (12), 1014.
- Parande, G., Manakari, V., Prasad, S., *et al.*, 2020. Strength retention, corrosion control and biocompatibility of Mg–Zn–Si/HA nanocomposites. *Journal of the Mechanical Behavior of Biomedical Materials* 103, 103584.
- Pathak, D.K., Pandey, P.M., 2020. Evaluation of in vitro corrosion behavior of zinc–hydroxyapatite and zinc–hydroxyapatite–iron as biodegradable composites. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 109 (3).
- Porter, F.C., 1994. *Corrosion Resistance of Zinc and Zinc Alloys*. CRC Press.
- Qian, C., Zhang, F., Sun, J., 2015. Fabrication of Ti/HA composite and functionally graded implant by three-dimensional printing. *Bio-Medical Materials and Engineering* 25 (2), 127–136.
- Radha, R., Sreekanth, D., 2017. Insight of magnesium alloys and composites for orthopedic implant applications – A review. *Journal of Magnesium and Alloys* 5 (3), 286–312.
- Ramirez, J.M., Hurt, W.C., 1977. Bone remodeling in periodontal lesions. *Journal of Periodontology* 48 (2), 74–77.
- Ratna Sunil, B., Sampath Kumar, T.S., Chakkingal, U., Nandakumar, V., Doble, M., 2014. Nano-hydroxyapatite reinforced AZ31 magnesium alloy by friction stir processing: a solid state processing for biodegradable metal matrix composites. *Journal of Materials Science: Materials in Medicine* 25 (4), 975–988.
- Rawal, S.P., 2001. Metal-matrix composites for space applications. *JOM* 53 (4), 14–17.
- Razavi, M., Fathi, M., Meratian, M., 2010. Microstructure, mechanical properties and bio-corrosion evaluation of biodegradable AZ91-FA nanocomposites for biomedical applications. *Materials Science and Engineering: A* 527 (26), 6938–6944.

- Rohatgi, P., 1991. Cast aluminum-matrix composites for automotive applications. *JOM* 43 (4), 10–15.
- Saberi, A., Bakhsheshi-Rad, H., Karamian, E., Kasiri-Asgarani, M., Ghomi, H., 2020. Magnesium-graphene nano-platelet composites: Corrosion behavior, mechanical and biological properties. *Journal of Alloys and Compounds* 821.153379.
- Salehi, M., Gupta, M., Maleksaedi, S., Sharon, N.M.L., 2018. Inkjet Based 3D Additive Manufacturing of Metals. *Materials Research Forum LLC*.
- Seah, K., Sharma, S., Girish, B., 1997. Corrosion characteristics of cast ZA 27 alloy reinforced with graphite particles. *Corrosion Science* 39 (1), 1–7.
- Shahin, M., Munir, K., Wen, C., Li, Y., 2020. Magnesium-based composites reinforced with graphene nanoplatelets as biodegradable implant materials. *Journal of Alloys and Compounds* 828.154461.
- Sharma, S., Somashekar, D., Satish, B., 2001. Effects of zircon particles on the corrosion behavior of zircon particles/ZA27 alloy composites. *Journal of Materials Processing Technology* 118, 1–3.
- Sharma, S., Seah, K., Satish, B., Girish, B., 1996. Effect of short glass fibers on the mechanical properties of cast ZA-27 alloy composites. *Materials & Design* 17 (5–6), 245–250.
- Sharma, S., Satish, B., Girish, B., Kamath, R., Asanuma, H., 1998. Dry sliding wear of short glass fibre reinforced zinc–aluminium composites. *Tribology International* 31 (4), 183–188.
- Shelley, J.S., LeClaire, R., Nichols, J., 2001. Metal-matrix composites for liquid rocket engines. *JOM* 53 (4), 18–21.
- Shivakumar, N., Vasu, V., Narasaiah, N., 2015. Synthesis and characterization of nano-sized Al_2O_3 particle reinforced ZA-27 metal matrix composites. *Procedia Materials Science* 10, 159–167.
- Shuai, C., Wang, B., Bin, S., Peng, S., Gao, C., 2020. Interfacial strengthening by reduced graphene oxide coated with MgO in biodegradable Mg composites. *Materials & Design* 191. 108612.
- Sietsema, W.K., 1995. Animal models of cortical porosity. *Bone* 17 (Suppl. 4), 297S–305S.
- Singerman, S., Jackson, J., Lynn, M., 1996. Titanium metal matrix composites for aerospace applications, Superalloys 1996. In: *Proceedings of Eighth International Symposium on Superalloys*.
- Singh, H., Hayat, M.D., Zhang, H., Cao, P., 2019. The decomposition of Si_3N_4 in titanium and its effect on wear properties. *Wear* 420–421, 87–95.
- Sivakumar, G., Ananthi, V., Ramanathan, S., 2017. Production and mechanical properties of nano SiC particle reinforced Ti–6Al–4V matrix composite. *Transactions of Nonferrous Metals Society of China* 27 (1), 82–90.
- Solomons, N.W., 2013. Update on zinc biology. *Annals of Nutrition and Metabolism* 62 (Suppl. 1), 8–17.
- Sravya, T.V.R.L., 2018. Futuristic In-situ and Ex-situ Approaches for Synthesis of Superior Magnesium Nanocomposites.
- Staiger, M.P., Pietak, A.M., Huadmai, J., Dias, G., 2006. Magnesium and its alloys as orthopedic biomaterials: A review. *Biomaterials* 27 (9), 1728–1734.
- Tekumalla, S., Yang, C., Seetharaman, S., *et al.*, 2016. Enhancing overall static/dynamic/damping/ignition response of magnesium through the addition of lower amounts (<2%) of yttrium. *Journal of Alloys and Compounds* 689, 350–358.
- Thostenson, E.T., Ren, Z., Chou, T.-W., 2001. Advances in the science and technology of carbon nanotubes and their composites: A review. *Composites Science and Technology* 61 (13), 1899–1912.
- Tsang, H.T., Chao, C.G., Ma, C.Y., 1997. Effects of volume fraction of reinforcement on tensile and creep properties of in-situ TiB/Ti MMC. *Scripta Materialia* 37 (9), 1359–1365.
- Tun, K.S., Gupta, M., 2007. Improving mechanical properties of magnesium using nano-yttria reinforcement and microwave assisted powder metallurgy method. *Composites Science and Technology* 67 (13), 2657–2664.
- Tun, K.S., Jayaramanavar, P., Nguyen, Q.B., *et al.*, 2013. Investigation into tensile and compressive responses of Mg–ZnO composites. *Materials Science and Technology* 28 (5), 582–588.
- Umeda, J., Kawakami, M., Kondoh, K., Ayman, E.L.S., Imai, H., 2010. Microstructural and mechanical properties of titanium particulate reinforced magnesium composite materials. *Materials Chemistry and Physics* 123 (2–3), 649–657.
- Weiner, S., Wagner, H.D., 1998. The material bone: Structure-mechanical function relations. *Annual Review of Materials Science* 28 (1), 271–298.
- Wang, F.-C., Zhang, Z.-H., Sun, Y.-J., *et al.*, 2015. Rapid and low temperature spark plasma sintering synthesis of novel carbon nanotube reinforced titanium matrix composites. *Carbon* 95, 396–407.
- Welsch, G., Boyer, R., Collings, E., 1993. *Materials Properties Handbook: Titanium Alloys*. ASM International.
- Wong, P.-C., Tsai, P.-H., Li, T.-H., *et al.*, 2017. Degradation behavior and mechanical strength of Mg–Zn–Ca bulk metallic glass composites with Ti particles as biodegradable materials. *Journal of Alloys and Compounds* 699, 914–920.
- Wong, W., Karthik, S., Gupta, M., 2005. Development of hybrid Mg/ Al_2O_3 composites with improved properties using microwave assisted rapid sintering route. *Journal of Materials Science* 40 (13), 3395–3402.
- Xin, Y., Hu, T., Chu, P.K., 2011. In vitro studies of biomedical magnesium alloys in a simulated physiological environment: A review. *Acta Biomaterialia* 7 (4), 1452–1459.
- Xinghong, Z., Qiang, X., Jiecai, H., Kvanin, V.L., 2003. Self-propagating high temperature combustion synthesis of TiB/Ti composites. *Materials Science and Engineering: A* 348 (1), 41–46.
- Xu, L., Pan, F., Yu, G., *et al.*, 2009. In vitro and in vivo evaluation of the surface bioactivity of a calcium phosphate coated magnesium alloy. *Biomaterials* 30 (8), 1512–1523.
- Yan, Y., Kang, Y., Li, D., *et al.*, 2017. Improvement of the mechanical properties and corrosion resistance of biodegradable $\beta\text{-Ca}_3(\text{PO}_4)_2/\text{Mg-Zn}$ composites prepared by powder metallurgy: The adding $\beta\text{-Ca}_3(\text{PO}_4)_2$, hot extrusion and aging treatment. *Materials Science and Engineering C: Materials for Biological Applications* 74, 582–596.
- Yan, Z., Chen, F., Cai, Y., Zheng, Y., 2014. Microstructure and mechanical properties of in-situ synthesized TiB whiskers reinforced titanium matrix composites by high-velocity compaction. *Powder Technology* 267, 309–314.
- Yang, H., Qu, X., Lin, W., *et al.*, 2018. In vitro and in vivo studies on zinc-hydroxyapatite composites as novel biodegradable metal matrix composite for orthopedic applications. *Acta Biomaterialia* 71, 200–214.
- Zhang, X., Zhang, Q., Hu, H., 2014. Tensile behaviour and microstructure of magnesium AM60-based hybrid composite containing Al_2O_3 fibres and particles. *Materials Science and Engineering: A* 607, 269–276.
- Zi-Run, Y., Hai-Xiang, H., Jiang, C.-F., *et al.*, 2017. Evaluation on dry sliding wear behavior of (TiB + TiC)/Ti–6Al–4V matrix composite. *International Journal of Precision Engineering and Manufacturing* 18 (8), 1139–1146.

Liquid Phase Processing of Metal Matrix Composites

Madhusoodhanan Geethakumari Akhil, Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India and Academy of Scientific and Innovative Research, Ghaziabad, New Delhi, India

Kaimanikal Madhurananthan Nair Sree Manu, Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India and Brunel University, London, United Kingdom

Thazhivilai Ponnu Devaraj Rajan, Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India and Academy of Scientific and Innovative Research, Ghaziabad, New Delhi, India

Ballambettu Chandrasekhara Pai, Council of Scientific & Industrial Research, National Institute for Interdisciplinary Science and Technology, Trivandrum, Kerala, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composites (MMCs) are the materials which offer high strength to weight ratio, high stiffness, conductivity, fracture toughness (Mavhungu *et al.*, 2017; Ramanathan *et al.*, 2019; Miracle, 2005). It has the ability to withstand the elevated temperature even in corrosive atmosphere making them an attractive selection in replacing conventional materials for several engineering applications (Schmidt *et al.*, 2004; Suresh *et al.*, 2012; Singh *et al.*, 2020). Normally the metal matrix materials of MMCs are aluminum alloys, titanium alloys, copper alloys and magnesium alloys, while the reinforcement materials are silicon carbide, aluminum oxide, boron carbide, graphite etc. in the form of fibers, whiskers and particles. Perhaps the single most important difference between fiber reinforced and particulate composites or conventional metallic materials is the directionality of properties. Particulate composites and conventional metallic materials are isotropic, while the fiber reinforced composites are generally anisotropic. Particulate reinforced composites offer higher ductility and their isotropic nature as compared to fiber reinforced composites makes them an attractive alternative. The metal matrix composites have various advantages over other types of composites. Such as high strength, high modulus, high toughness and impact properties, Low sensitivity to changes in temperature or thermal shock, high surface durability and low sensitivity to surface flaws, high electrical conductivity. The inclusion of high strength and modulus ceramic reinforcements to a ductile metal matrix forms the metallic composites having unique combination of properties offering high resilience, high-temperature applications compared to polymer and ceramic matrix composites. From tribological perspective, the addition of hard ceramic reinforcements increases the wear resistance of the metallic matrix. Ultimate combination of properties of MMCs depends on a number of factors related to matrix, reinforcement, processing, and heat treatment (Singh *et al.*, 2020). The properties of MMC includes (1) high toughness and high impact properties (2) high thermal and electrical conductivities (3) excellent anti-abrasion, antifriction (4) excellent *machinability* (5) reduced wear (6) lightweight materials (7) good specific stiffness and strength (8) high in strength and (9) low ~~in~~ density.

Constituents and Classification of MMCs

Metal matrix composites can be classified in various ways. We may classify composites on the basis of the type of matrix employed in them for example, polymer matrix composites (PMCs), metal matrix composites (MMCs), and ceramic matrix composites (CMCs). We may also classify composites on the basis of the type of reinforcement they employ (Meyers and Chawla, 2008; Clyne and Withers, 1995). They are (1) Particle reinforced composites (2) Short fiber, or whisker reinforced, composites. (3) Continuous fiber, or sheet reinforced, MMCs and (4) Laminate composite (see Fig. 1).

Processing Methods of MMC

Metal matrix composite materials can be produced by many different techniques. The focus of the selection of suitable process engineering is the desired kind, quantity and distribution of the reinforcement components (particles and fibers), the matrix alloy and the application. By altering the manufacturing method, the processing and the finishing, as well as by the form of the reinforcement components it is possible to obtain different characteristic profiles, although the same composition and amounts of the components are involved. The production of a suitable precursor material, the processing to a construction unit or a semi-finished material (profile) and the finishing treatment must be separated. For cost effective reasons prototypes, with dimensions close to the final product, and reforming procedures are used, which can minimize the mechanical finishing of the construction units.

Development of fabrication processes for the production of high-performance composites has been reported in many research studies. The methods which are commonly used for fabrication of the MMCs are (1) Solid-phase processing and (2) Liquid-phase processing (Bains *et al.*, 2016).

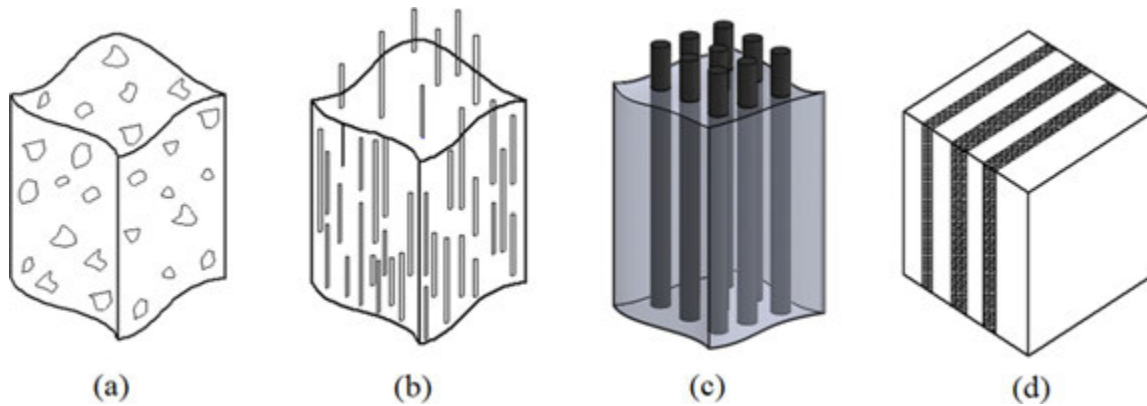


Fig. 1 Schematic presentation of (a) particle reinforcement; (b) short fiber reinforcement; (c) continuous fiber reinforcement; (d) laminate reinforcement.

The adoption of the route for the synthesis of MMCs depended on many factors including the matrix temperature during processing, extent and reinforcement loading, and desired degree of microstructural integrity. Well-established methods in solid-state processes include blending of powder followed by isostatic pressing (powder metallurgy (PM) processing), spray deposition techniques, and diffusion bonding. Melt stir casting, melt infiltration, spray casting, and in situ (reactive) processing come from liquid-state processing (Bains *et al.*, 2016). Other techniques include in situ processes and two phase (solid-liquid) processes.

Liquid State Fabrication of Metal Matrix Composites

The molten matrix and reinforcements are *unified* together by solidification mechanism (Sahu and Banchhor, 2016). In the liquid state casting technique, the particulates are mechanically well distributed over the liquid metal before casting and solidification (Estrada-Guel *et al.*, 2009). These methods are typically cost effective (Kerti and Toptan, 2008). The following are the various processing methods which come under liquid state fabrication techniques.

Stir Casting Process

Stir casting is the most economical and commercially adopted technique for the production of metal matrix composites. It is also known as “vortex technique” (Attar *et al.*, 2015). In this technique, reinforcing phases (ceramic particles, short fibers/whiskers) are introduced in to the molten metal by means of mechanical stirring (Fig. 2). In 1968 Ray initiated the stir casting of particulate aluminum metal matrix composite by introducing alumina (Al_2O_3) particles in to molten aluminum alloy by mechanical stirring (Giot *et al.*, 1987). The agglomeration of particles during fabrication is the major drawback of stir casting process (Nienow *et al.*, 1997). If the dispersion of reinforcement particles is not uniform, then they have high tendency to agglomeration and clustering. If the reinforcement particles are *not stirred properly* in molten matrix, they *will* tend to sink or float to the molten melt due to the density differences between the reinforcement particles and the matrix alloy melt. By injecting the reinforcement particles with the aid of an inert gas supply into the melt helps in improving the distribution of the particles (Hashim *et al.*, 1999).

Many research studies suggested that reinforcement in particulate form up to 30% by weight can be added in molten alloy, to achieve better distribution of the reinforcement (Luo, 1995). Reinforcement particles are added in to the molten aluminum alloy and the homogeneity of the added particulates during solidification of composite depends on following factors; (a) Stirring speed and time (b) Stirring blade angle (c) Pouring temperature and solidification rate (d) Reinforcement’s size, percentage and its relative density.

Compocasting Process

In recent years, researchers have identified compocasting as one of the economic and efficient methods for fabricating aluminum matrix composites (AMC) over other conventional methods due to its advantages like low casting temperature, uniform distribution of reinforcement without agglomeration, good wettability and better matrix-reinforcement bonding (Rosso, 2006). Compocasting is a solid-liquid state method in which a vortex is created in the semisolid molten metal (between the solidus and liquidus temperature of the matrix alloy) using an impeller driven by an electric motor, and the reinforcements are added into the vortex under stirring. During compocasting process, the higher viscosity of semisolid molten metal slurry transmits shear force over the agglomerated reinforcements which lead to better dispersion and distribution of reinforcement in the matrix. Both the micron and nano size reinforcements are successfully incorporated into the matrix by compocasting process.

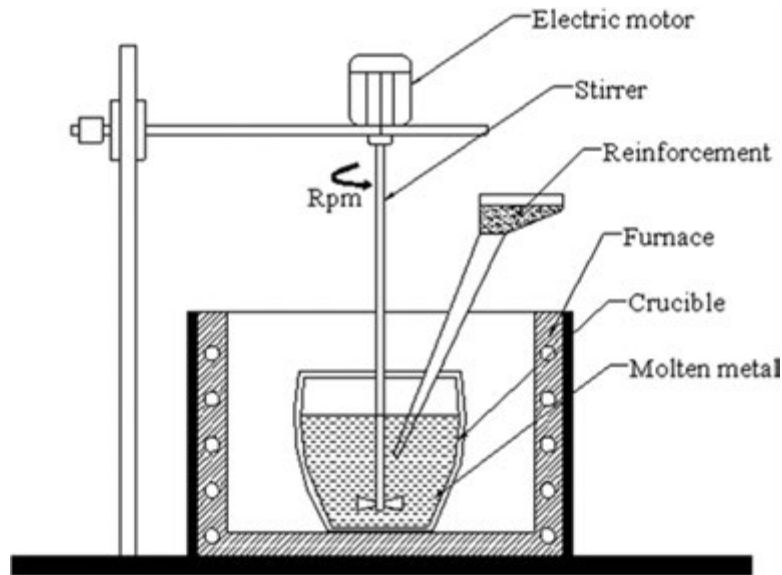


Fig. 2 Schematic diagram of stir casting process.

The major process parameters considered during compocasting process are (1) crucible size (2) size and shape of the stirrer (3) semisolid metal temperature (4) stirring time (5) stirring speed (6) mold temperature and (7) reinforcement feeding rate. The properties of the final composite depend on the aforesaid process parameters (Kok, 2005). The compocasting process has two variations namely semisolid–semisolid (SS) and semisolid–liquid (SL) routes, in which the matrix alloy during casting step is either in partially liquid or in fully liquid state respectively. However, during compocasting process the matrix will be in the semi-solid state for both the variations and the reinforcements are added into it. Both the variations have its advantages and disadvantages, some of the benefits of SS route are (1) low processing temperature (2) lower interfacial reaction (3) low solidification shrinkage, etc. While considering the benefits of SL route they are (1) ease of casting, (2) less porosity etc. (Akhlaghi *et al.*, 2004).

Spray Deposition

Fabrication of composite by spray forming process involves melting of an alloy in a furnace, forcing the melt through a small orifice, passing a stream of compressed inert gas, injecting reinforcement through the jet and breaking the liquid metal into fine semi solid droplets. These semi solid droplets are deposited over a stationary substrate to form solid preform (Fig. 3). It is difficult to attain uniform distribution of reinforcements into the metal matrix by this method but the composites formed by spray deposition process are not very expensive (White *et al.*, 1987).

Disintegrated Melt Deposition Technique (DMD Technique)

DMD technique is a liquid-state processing method, which is more suitable for the fabrication of nano composites. This technique has the combined advantages of gravity die casting and spray deposition technique (Gupta and Sharon, 2011). The DMD process offers higher superheat temperatures and lower impinging gas jet velocity which attribute to uniform distribution of nano sized reinforcement particles with the absence of agglomeration, minimum interaction time of nanoparticles with matrix in the molten state, elimination of impurities/oxides (Ceschini *et al.*, 2016). This process involves addition of nano ceramic particles by mechanical stirring into the molten metal/alloy with an impeller. The composite slurry thus formed is then allow to exit from the bottom of the crucible through a nozzle, followed by disintegration of melt by jets of inert gas at a superheat temperature of 750°C and is finally deposited onto a metallic substrate (Fig. 4). The disintegration of composite melt ensures higher solidification rate and fine-grained structure. This processing technique can be employed for the fabrication of aluminum and magnesium nano composites (Jayalakshmi *et al.*, 2016).

The main challenges of this process are (1) Not suitable to produce cast components as the method is suitable to produce Metal Matrix Nano Composite ingots to be used as precursors for making wrought products, (2) difficult to be automated and to be used for continuous casting operations unless modifications are made in equipment design.

In-Situ Processing

In-situ synthesis is a process wherein the reinforcements are formed in the matrix by controlled metallurgical reactions with various reinforcement ceramic particles such as SiC, AlN and TiC (Zawrah and Aly, 2006; Daoush *et al.*, 2015; Nie *et al.*, 2014). In

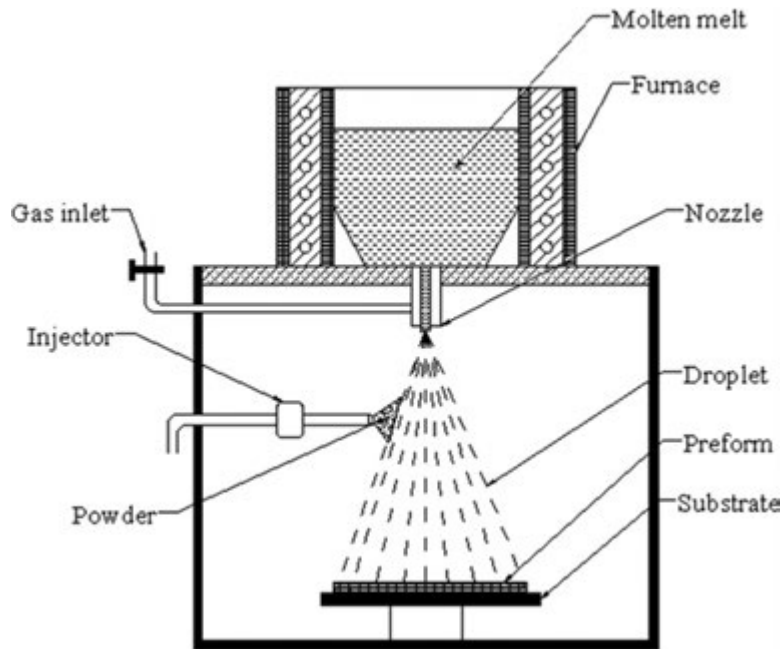


Fig. 3 Schematic diagram of spray forming process.

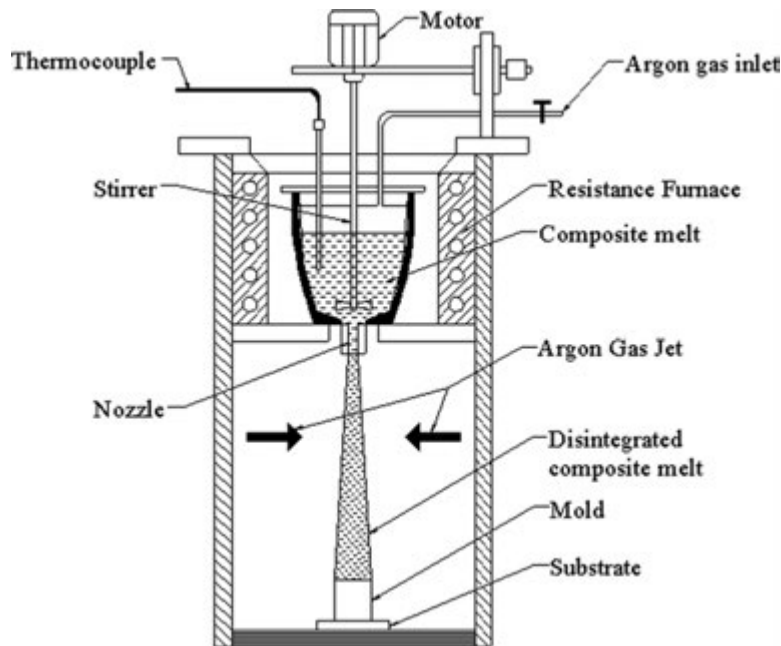


Fig. 4 Schematic diagram of DMD process.

this process, a reinforcement phase is introduced in the matrix phase as an outcome of precipitation from the melt while it cools and solidifies. During fabrication, one of the reacting elements is usually a constituent of the molten matrix alloy. The other reacting elements may be either externally-added fine powders or gaseous phases, final reaction products is the reinforcement dispersed in matrix alloy (**Fig. 5**). It is difficult to disperse the reinforcing particles uniformly in metal melts due to the low wettability with the melt (**Jamaati and Toroghinejad, 2010**). The main difficulty in the process is the reaction of particle size of less than 1 mm, particle agglomeration and serious health hazards (**Changizi, 2005**). The interface bonding may be lowered due to the porosity and segregation at the interface between the matrix and reinforcement (**Aghajanian et al., 1991**). It requires the higher reaction time temperature and longer holding time *which greatly increases the cost of production*.

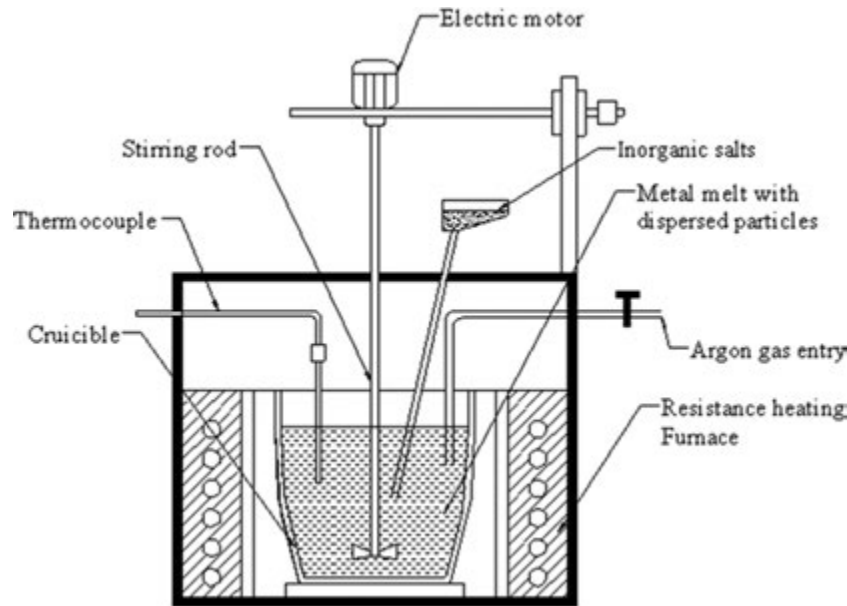


Fig. 5 Schematic diagram of in situ direct reaction synthesis apparatus.

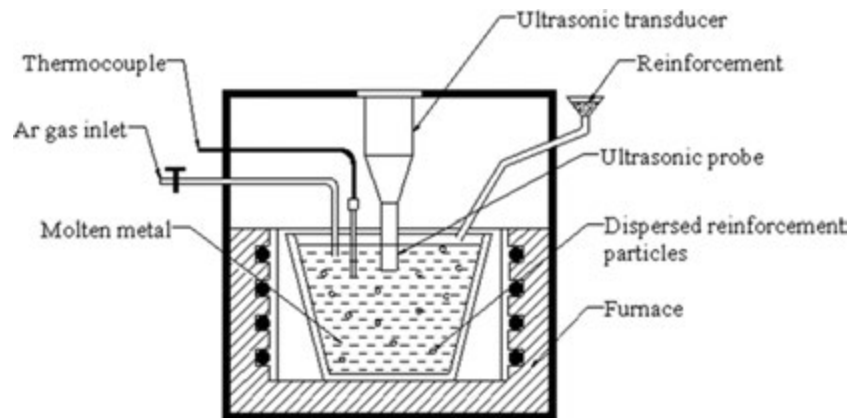


Fig. 6 Schematic diagram of the electromagnetic melt stirring apparatus with ultrasonic vibration.

Ultrasonic Processing

There are mainly two types of ultrasonic processing system have been used for the manufacturing of metal matrix composites, these are contact (Yang *et al.*, 2004; Yang *et al.*, 2004) and noncontact-type (Padhi and Kar, 2011). In case of contact-type, the ultrasonic probe is dipped into the liquid melt that directly aids to disperse the micro or nano reinforcement particles in the melt and the developed slurry is subsequently solidified by conventional casting route. Whereas in noncontact-type, solidification of liquid melt with added nanoparticles is performed in an ultrasonic chamber (Padhi and Kar, 2011). The contact-type system is the most preferred system by considering its simplicity in operation and effectiveness to disperse nano/micro particles in melt. A typical contact-type Ultrasonic processing apparatus is schematically illustrated in Fig. 6.

The ultrasonic processing involves mainly two important phenomena, i.e., transient cavitation and acoustic streaming (Yang *et al.*, 2004; Li *et al.*, 2004). The acoustic cavitation is initiated by the high-intensity ultrasonic waves (above 25 W/cm^2) that generate strong non-linear effects in the molten metal (Yang *et al.*, 2004; Yang *et al.*, 2004; Borgonovo and Apelian, 2011). The effect of such cavitation includes the formation, growth, pulsating, and collapsing of micro air bubbles that tend to be trapped inside nanoparticle clusters during the negative and positive pressure cycles (Choi *et al.*, 2012). The strong cavitation can create transient (in the order of nanoseconds) micro "hot spots" that generate temperature of about 5000°C , pressure of above 1000 atms, and heating and cooling rates above 1010 K/s (Cao *et al.*, 2008; Li *et al.*, 2007). The severe implosive impact in conjunction with local transient high temperature can effectively fracture nano/micro particle clusters, clean the particle surface and enhance the wettability between melts

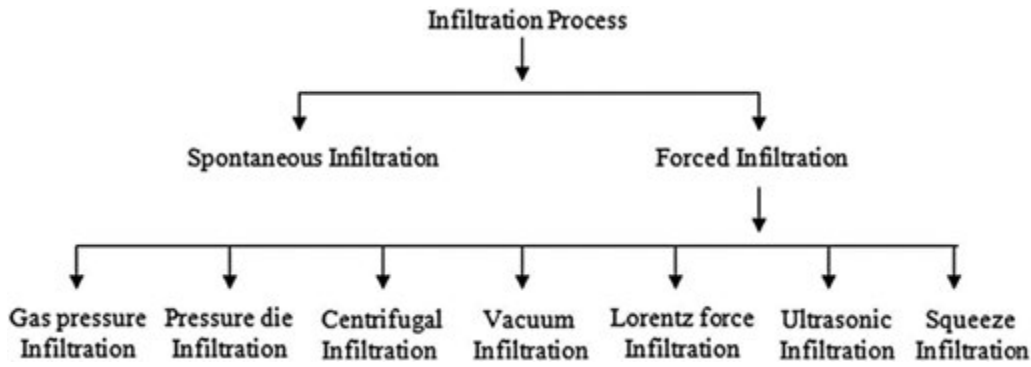


Fig. 7 Classification of infiltration process for the fabrication of metal matrix composites.

and particulates (Yang *et al.*, 2004; Li *et al.*, 2004). Acoustic streaming flows throughout the melt and helps to circulate nano/micro particles all over the melt. Compared to conventional castings, Ultrasonic processing technique proves to be more reliable for producing nanocomposites even with system having extreme difference in thermal coefficients between metal matrix and ceramic particulates (Li *et al.*, 2007).

Liquid Metal Infiltration

Liquid metal infiltration of ceramic preform is one of the best suited processing technique to produce metal matrix composite components with high volume fraction of reinforcement. Through this method it is possible to fabricate *composites* with variety of complex shapes. Infiltration is a liquid-state fabrication method, in which a porous preform (reinforcement) made of ceramic particles, fibers, woven etc. are impregnated in a molten matrix metal, which fills the pores between the dispersed-phase inclusions. Synthesis of porous ceramic preform with sufficient mechanical strength, uniform pore distribution, pore size, and porosity level is one of the crucial steps involved in the infiltration processing of composites (Manu *et al.*, 2016). Some of the important fabrication methods for porous ceramic foams are polymer replica techniques, gel casting, direct foaming of suspensions, and using pore-forming agents (PFA) (Colombo and Hellmann, 2002; Sepulveda, 1997; Montanaro *et al.*, 1998). Al, Mg, and Cu based alloys have been successfully used as matrices to fabricate MMCs through liquid infiltration, as they can be easily melted and handled in the liquid state. Difference from one infiltration method to another is based on the technique that is used to drive the molten metal to enter the preform.

The liquid infiltration processes can be broadly classified into two categories: (1) spontaneous infiltration and (2) forced infiltration (Fig. 7). When capillary action of the reinforcement phase acts as a driving force for infiltration, the category of processes is termed as spontaneous infiltration. In forced infiltration an external pressure such as gaseous, mechanical, squeeze, electromagnetic etc. are applied to the liquid matrix phase which accelerates the infiltration of molten metal through the preforms. The processing details are explained here.

Spontaneous/pressure-less infiltration

In spontaneous infiltration, the molten liquid metal invades into the voids of the porous body without the application of any external forces (Fig. 8). This can be accomplished with the help of controlled temperature and gas atmosphere ensuring good wetting conditions are maintained for self-permeation (Lee *et al.*, 2009).

Forced Infiltration

The infiltration process in which the aid of an external pressure or mechanical force governs the infiltration of liquid metal into the porous reinforcement is called forced infiltration. Poor wetting between the molten metal and porous structure can be overcome by endowing mechanical energy to force the metal into the porous preform. There are various types of forced infiltration methods and these are described below.

Gas pressure infiltration

An infiltration process in which pressurized gas (Fig. 9) is used as driving force for the penetration of molten metal into the porous body. Gas infiltration process is normally carried out in combination with vacuum at the other end of the preform to get rid of entrapped air to facilitate easy penetration at lower gas pressures (Carreno-Morelli *et al.*, 1998). As a result, high pressure is needed for complete infiltration of molten metal, hence, anti-pressure of gases is to be considered during the analysis of threshold pressure. With the ideal gas equation $PV = nRT$, the anti-pressure of gas can be expressed as (Qi *et al.*, 2012)

$$p_g(z) = \frac{p_0 T_z L}{T_0 [L - Z]}$$

where p_0 is the pressure of gas at initial time, T_0 is the initial time temperature, L is the preform total length, and T_z is the

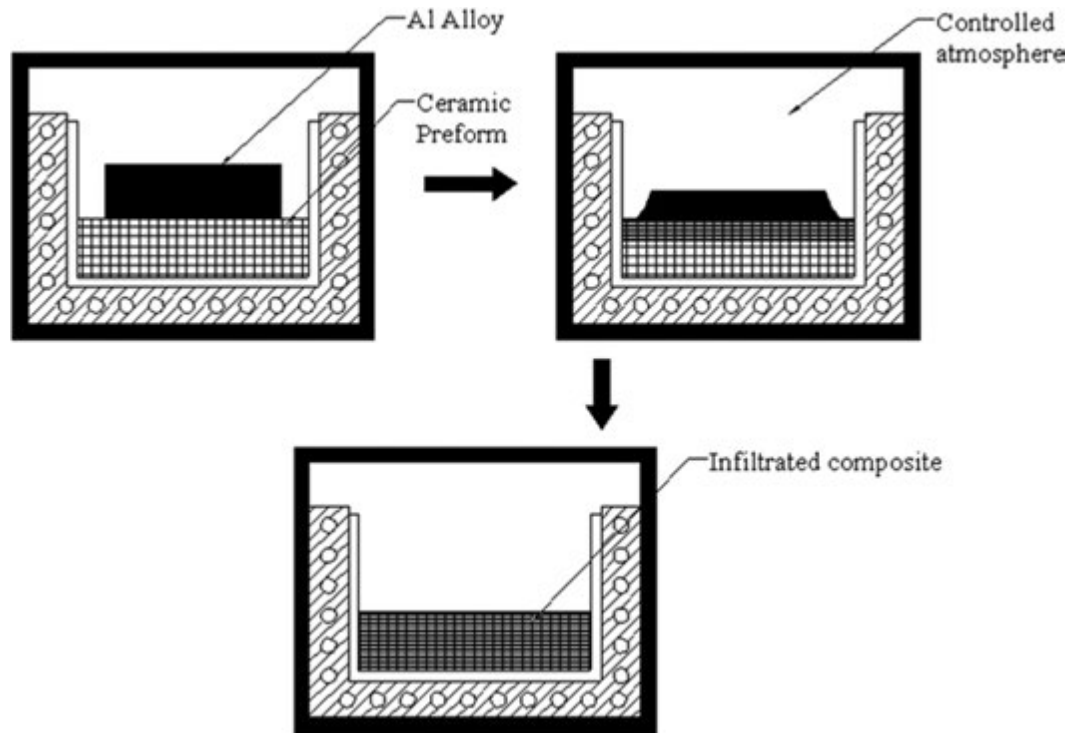


Fig. 8 Schematic diagrams showing the working principle of spontaneous infiltration process: (a) infiltration takes place at controlled atmosphere, (b) progressiveness of infiltration, and (c) final composite.

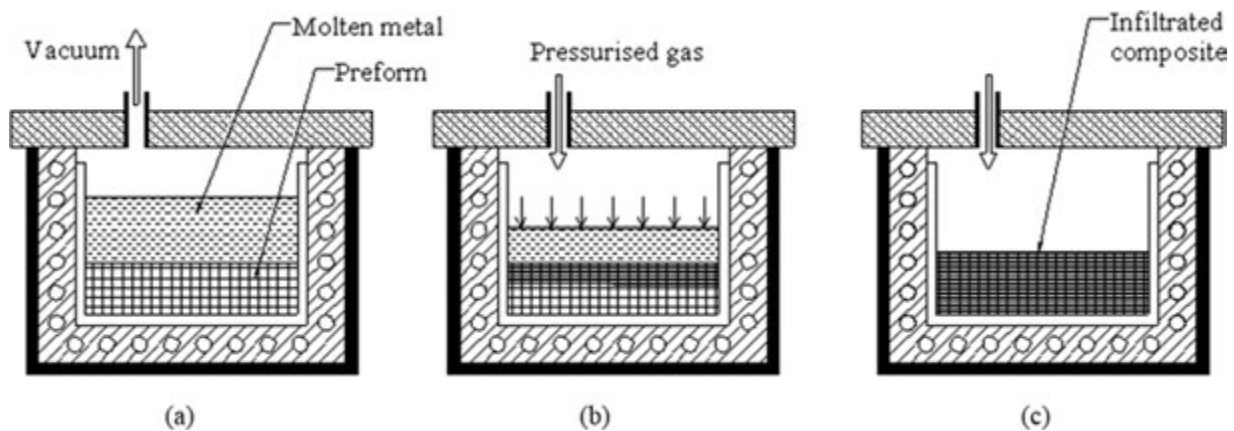


Fig. 9 Schematic illustrations of gas pressure infiltration process for the fabrication of MMCs: (a) infiltration process carried out with vacuum to remove the entrapped air in the preform to facilitate easy molten metal penetration, (b) applying pressurized gas as a driving force for metal infiltration, and (c) final composite.

temperature of the gas when the infiltration attains a height z . Enhance in the infiltration temperature and pressure during gas pressure infiltration process improves the relative density of the component, which shows an effect on the mechanical properties of the final composite (Manu *et al.*, 2016).

Pressure die infiltration

Pressure die infiltration process involves placing a porous preform inside a solid die and applying pressure with the help of a movable piston to allow penetration of liquid metal in the porous preform (Fig. 10 (a) and (b)). Process parameters that are optimized include speed, die temperature, and pressure of the piston. Main advantages of this process are low cost and ability to fabricate components of high complexity and precision. The deformation of preform due to the pressure of the molten metal

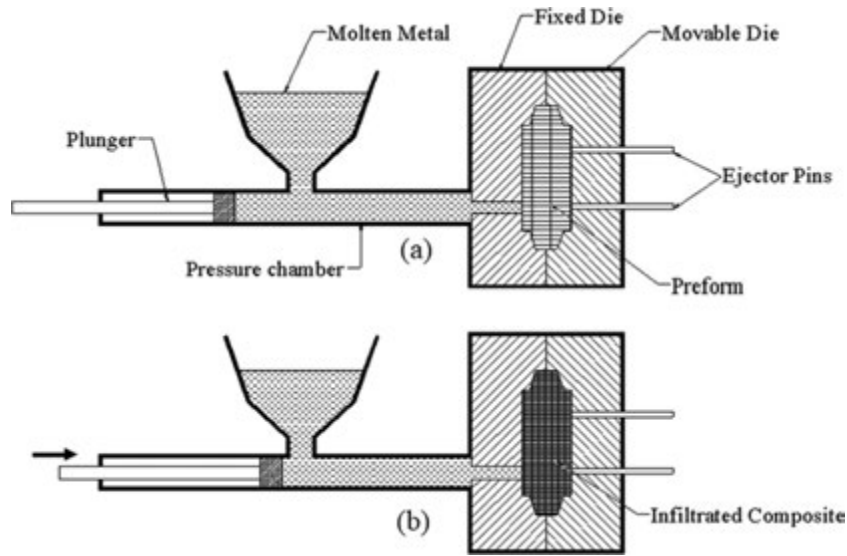


Fig. 10 Schematic diagrams of pressure die infiltration process for the fabrication of MMCs: (a) before applying pressure to molten metal using plunger and (b) after applying pressure to molten metal using plunger to form the composite.

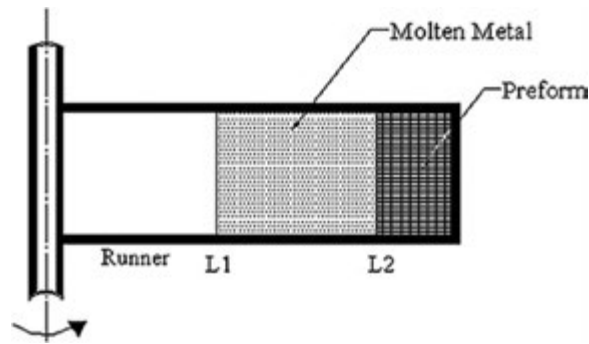


Fig. 11 Schematic of a conventional centrifugal infiltration process.

before and during infiltration will be high for pressure die casting compared to squeeze casting owing to high compression rate of preform during infiltration.

Centrifugal infiltration

In centrifugal infiltration process, rotational/centrifugal force is used to infiltrate porous preform with liquid molten metal. During the fabrication of composites, porous reinforcement material is positioned inside a mold (at the end) having an elongated runner, which was filled with molten metal. Large rotational velocities of the runner initiate centrifugal force with required drive for infiltration to overcome the threshold pressure for melt penetration and viscous forces of the molten metal to flow in the preform. (Fig. 11). The molten metal pressure exerted on the porous preform during centrifugal force is given by (Wannasin and Flemings, 2005)

$$P_c = \frac{1}{2} \rho \omega^2 (L_2^2 - L_1^2)$$

where ρ is the density of molten metal, $\omega = \frac{2\pi N}{60}$, N is the rotational speed in rpm, and L_2 and L_1 are the outer and the inner molten metal's level from the rotation axis.

Lorentz force infiltration

Lorentz force infiltration process is a novel infiltration process in which electromagnetic force is used to propel the molten metal into the ceramic preforms. During the process, the preform gets immersed in a liquid molten metal which is subjected to a high-frequency magnetic pulse. Simultaneously, eddy current persuaded in the liquid metal gets to interact with the magnetic pulse and develop a Lorentz body force in the liquid molten metal causing the liquid metal to enter into the ceramic preform at a high speed.

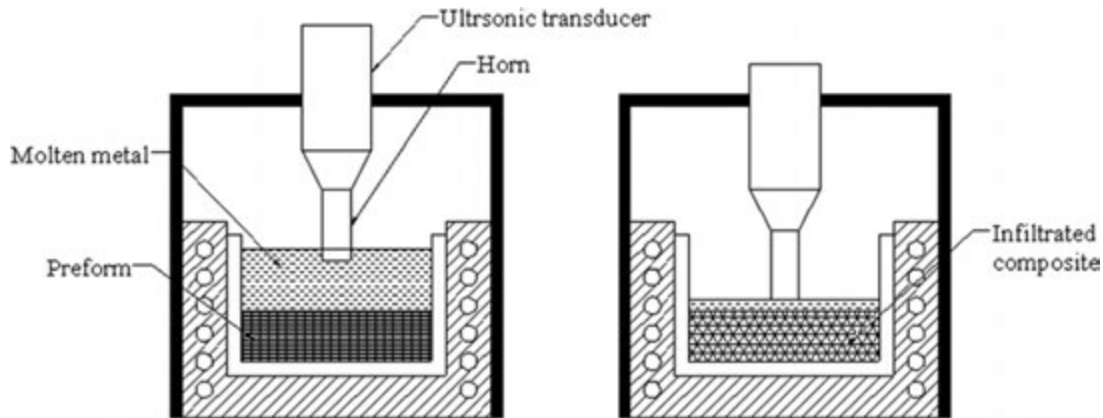


Fig. 12 Schematic diagram of the ultrasonic vibration apparatus.

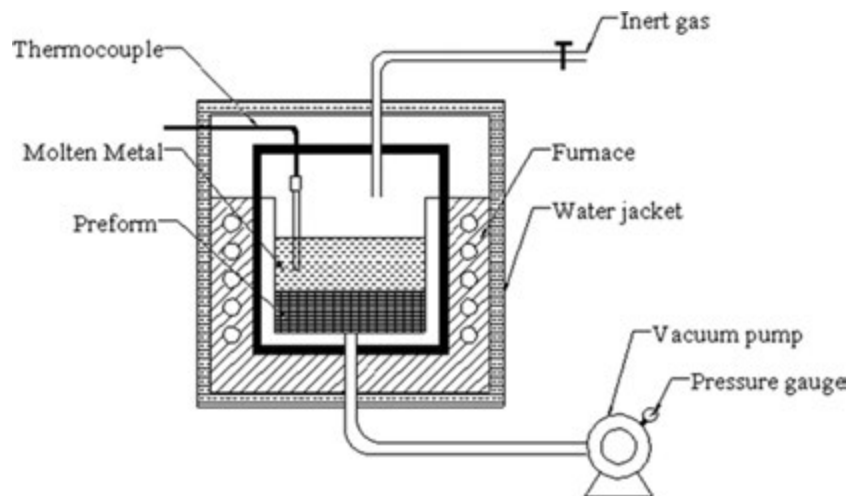


Fig. 13 Schematic diagram showing the working principle of vacuum infiltration process for the fabrication of MMCs.

Andrews and Mortensen had successfully fabricated void-free aluminum/ Al_2O_3 fiber composite by Lorentz force infiltration technique. They suggested that the infiltration depth depends on the nature and number of discharges (Mortensen and Jin, 1992).

Ultrasonic infiltration

In ultrasonic infiltration process, pressure waves generated by the ultrasonic vibration assist in the penetration of the molten matrix material in the ceramic preform. When ultrasonic vibration is actuated through a horn in the liquid molten metal, acoustic cavitations (bubbles) are originated. The air entrapped in the porous preform and the dissolved gas in the molten metal can become the cavitations' nuclei. When a bubble collapses shock wave originates close to the molten metal resulting in infiltration process (Fig. 12) (Pan *et al.*, 1995; Deming *et al.*, 1993). The important process parameters considered for the ultrasonic infiltration is ultrasonic power, hole in the horn, and fabrication speed. Increase in the diameter of the hole in the horn decreases the infiltration ratio due to the depletion in the formation of acoustic cavitations and studies show that optimum diameter of the hole is 5 mm. The system which undergoes ultrasonic vibration shows reduction in contact angle due to heavy vibration acceleration and thereby improving wettability (Sasaki *et al.*, 2005).

Vacuum infiltration

Vacuum infiltration involves a negative pressure infiltration in which matrix metal gets penetrated into the evacuated preform due to the application of suction pressure (Fig. 13). Process parameters like infiltration temperature, infiltration time, and applied vacuum ($\sim 300\text{--}500$ mmHg) play a crucial role in this process (Gul and Acilar, 2004). Infiltration rate gets increased with increasing the molten metal temperature and by applying coating on the reinforcement, thereby reducing the infiltration incubation period to avoid brittle interfacial reactions (Chung *et al.*, 1999). Low solidification rate of the final component during processing can be stepped up as one of the disadvantage of vacuum infiltration which enhances the grain growth of the matrix metal and interfacial reaction between matrix and the reinforcement (Yang and Chung, 1989). To avoid the liquid molten metal

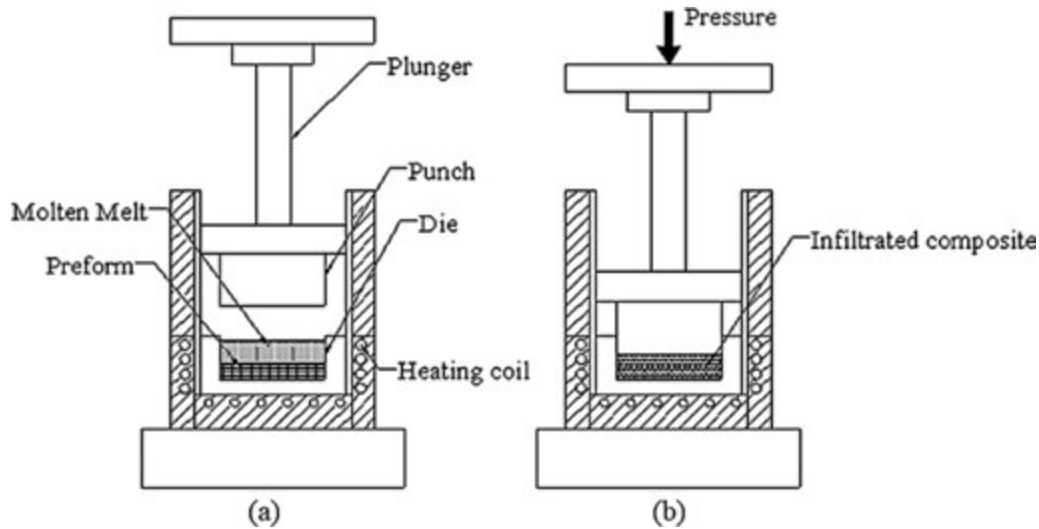


Fig. 14 Schematic diagrams of squeeze infiltration process for the fabrication of MMCs: (a) before the application of squeeze pressure and (b) after the application of squeeze pressure as a driving force to infiltrate molten metal into the preform.

getting into the vacuum pump by chance during infiltration process one portion of the connection pipe is filled with metal chips, so that the molten metal entering into the pipe gets solidified in that particular area without damaging the vacuum pump. Studies have shown that Al and Mg based composite materials with more than 50 vol pct reinforcement can be successfully fabricated using vacuum infiltration technique (Xiong *et al.*, 2011).

Squeeze infiltration

Squeeze infiltration is one of the widely used method for the production of near net shape metal matrix composites with close control over shape, volume fraction, chemistry, and distribution of reinforcement (Beffort *et al.*, 2007; Rohatgi *et al.*, 2006; Deqing *et al.*, 2001). This process offers advantages over other conventional methods for fabricating composite components which are difficult to be machined. The process involves the formation of porous preform as the reinforcement and its infiltration with the molten matrix material under pressure (Fig. 14) typically in the range of 50–100 MPa (Mortensen, 2000). The appropriate magnitude of applied pressure ensures eradication of porosities, refined microstructure, enhanced processing speed, and termination of chemical reactions. For the development of quality composites processing parameters of squeeze infiltration have to be optimized.

Applications

The automotive market represents the largest current market for Aluminum MMCs on a volume basis. The potential for AlMMCs in this area is barely tapped, however, and represents a great opportunity for substantial growth. Through R&D, lighter, engineered materials are being developed which offer better performance than the existing materials. Replacement of steel and cast iron in internal combustion engine applications as well as in unsprung weight components, such as the brake system, is judged the most promising for the near term. Aluminum metal matrix composites are suitable replacements, not only for steel but also for aluminum alloys in various automotive systems and components. Aluminum-based engine blocks, suspension components, body panels and frame members are increasingly becoming common (Lutsey, 2010). Aluminum alloys and composites are also competing to replace many various traditional steel components in vehicles, such as valve covers, torque converter and transmission housings, crankcase, control arms, cradles, suspension links, door frames, steering wheels, dashboards, sheet panels and beams are also being replaced by alloy aluminum alloys and composites (Caceres, 2007).

Aluminum alloys and composites have played a big role in the advancement of aircraft and rocket technology. Aluminum alloys and/or composites are the favored choice for the fuselage, wing and supporting structures of commercial airliners and military or cargo aircraft. Aluminum metal matrix composites have been the material of choice for space structures of all types ever since the launch of Sputnik 1 (October 4, 1957). Chosen for their light-weight and their ability to withstand the stresses that occur during launch and operation in space, AlMMCs and alloys have been used on Apollo spacecraft, the Skylab, the space shuttles and the International Space Station. Aluminum alloys/composites consistently exceed other metals in such areas as mechanical stability, dampening, thermal management and reduced weight (Finckenor, 2017).

The University of Wisconsin-Milwaukee (UWM) reportedly developed aluminum alloy pistons and cylinder liners containing dispersed graphite particles that provide solid lubrication (Macke *et al.*, 2012). The graphite-containing aluminum has a lower friction coefficient and wear rate and does not seize under boundary lubrication. Aluminum/graphite pistons and liners were

tested in gas and diesel engines and in race cars, and the results showed reduced friction coefficients and wear rates. The friction coefficient of Al-graphite composites was measured and found to be as low as 0.2 (Rohatgi *et al.*, 1992). This makes it a suitable material for cylinder liners in light-weight aluminum-engine blocks, for its ability to enable engines reach operating temperatures more quickly while providing superior wear resistance, improved cold start emissions and reduced weight (Gumus, 2009). Aluminum-based composite liners can be cast in situ using conventional methods, including sand, permanent mold, die casting and centrifugal casting.

Components such as control arms or wheel hubs made of strong silicon carbide (SiC)-reinforced aluminum or aluminum nanocomposites can further improve aluminum alloy designs by enhancing strength while using less material than similar aluminum arms (Withers and De Waas Tilakaratna, 2005).

Heat sinks play two key roles in electronic packaging: thermal management and mechanical support. Heat sinks support electronic devices and provide a path for heat dissipation. They are used in packages and with printed circuit boards (PCBs). Traditional heat sinks were primarily aluminum, copper or unalloyed blends of two metals, such as copper-tungsten or copper-molybdenum. The traditional heat sinks have exhibited a number of shortcomings, which has necessitated designing of new improved materials, primarily composites reinforced with fibers and particles. The new materials exhibit better properties including high thermal conductivities; low, controllable coefficients of thermal expansion; weight reductions; high strength and stiffness; and availability of net-shape fabrication processes. Utilization of composite materials is not a new phenomenon in electronic packaging. Aluminum metal matrix composites with the high volume fraction of reinforcement are attractive materials for thermal management. This is in view of the possibility to further enhance the thermal conductivity (TC) of the composite material by the use of high TC reinforcements and the flexibility to adjust the CTE by controlling the volume fraction of the reinforcement. Aluminum and copper were usually used as matrices due to their high TCs, and the reinforcements involved SiC, carbon and diamond. However, owing to the fact that the specific thermal conductivity of aluminum-based composites was higher than that of Cu-based composites, aluminum-based composites are more desirable in avionic applications where light-weight is demanded (Zweben, 2005).

Conclusion and Future Scope

MMCs are the material exhibiting properties that are hard to be obtained from monolithic material. The use of metal matrix composites is increasing day by day due to their characteristics of behavior with their high strength to weight ratio. These can be tailored and used as per the demands of various industrial applications by suitable fusion of their constituent materials. Every industry like automobile, sports, aerospace, thermal packaging, construction, marine, etc., utilizes the benefits of composites especially metal matrix composites. Various processes like stir casting, compo-casting, liquid metal infiltration etc., are used to manufacture MMCs as discussed in this article. Fabrication of MMCs determines the correlation between properties and cost of the material for a given set of constituents. Compatibility between matrix and reinforcement is a significant necessity for fabrication.

Each combination can be easily processed into useful composites. However, some research investigations suggest that tailoring the metal matrix interfaces is possible in order to cope with compatibility. Economical fabrication techniques, less costly materials, and judicious surface modification methods should be given attention as research and development priorities.

Acknowledgment

The authors would like to thank the Director and Members of CSIR-NIIST for the support and encouragement, DST and IGSTC (NearNetMAC) for the funding.

References

- Aghajanian, M.K., Rocazella, M.A., Burke, J.T., Keck, S.D., 1991. The fabrication of metal matrix composites by a pressureless infiltration technique. *Journal of Materials Science* 26 (2), 447–454. Jan 1.
- Akhlaghi, F., Lajevardi, A., Maghanaki, H.M., 2004. Effects of casting temperature on the microstructure and wear resistance of compocast A356/SiCp composites: A comparison between SS and SL routes. *Journal of Materials Processing Technology* 155, 1874–1880. Nov 30.
- Attar, S., Nagaral, M., Reddappa, H.N., Auradi, V., 2015. A review on particulate reinforced aluminum metal matrix composites. *Journal of Emerging Technologies and Innovative Research* 2 (2), 225–229.
- Bains, P.S., Sidhu, S.S., Payal, H.S., 2016. Fabrication and machining of metal matrix composites: A review. *Materials and Manufacturing Processes* 31 (5), 553–573.
- Beffort, O., Long, S., Cayron, C., Kuebler, J., Buffat, P.A., 2007. Alloying effects on microstructure and mechanical properties of high volume fraction SiC-particle reinforced Al-MMCs made by squeeze casting infiltration. *Composites Science and Technology* 67 (3–4), 737–745.
- Borgonovo, C., Apelian, D., 2011. Manufacture of aluminum nanocomposites: A critical review. In: Ceschini, L., Montanari, R. (Eds.), *Materials Science Forum*, vol. 678. Trans Tech Publications Ltd, pp. 1–22.
- Caceres, C.H., 2007. Economical and environmental factors in light alloys automotive applications. *Metallurgical and Materials Transactions A* 38 (7), 1649–1662.
- Cao, G., Konishi, H., Li, X., 2008. Mechanical properties and microstructure of SiC-reinforced Mg-(2, 4) Al-1Si nanocomposites fabricated by ultrasonic cavitation based solidification processing. *Materials Science and Engineering A* 486 (1–2), 357–362.

- Carreno-Morelli, E., Cutard, T., Schaller, R., Bonjour, C., 1998. Processing and characterization of aluminium-based MMCs produced by gas pressure infiltration. *Materials Science and Engineering A* 251 (1–2), 48–57.
- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2016. *Aluminium and Magnesium Metal Matrix Nanocomposites*. Singapore: Springer Nature.
- Changizi, A., 2005. *Production and Properties of In-Situ Aluminum Titanium Diboride Composites Formed by Slag-Metal Reaction Method* (Doctoral dissertation). Middle East Technical University.
- Choi, H., Konishi, H., Li, X., 2012. Al_2O_3 nanoparticles induced simultaneous refinement and modification of primary and eutectic Si particles in hypereutectic Al–20Si alloy. *Materials Science and Engineering A* 541, 159–165.
- Chung, W.S., Chang, S.Y., Lin, S.J., 1999. Low volume fraction SiC p/AA 380.0 composites fabricated by vacuum infiltration. *Journal of Materials Research* 14 (3), 803–810.
- Clyne, T.W., Withers, P.J., 1995. *An Introduction to Metal Matrix Composites*. Cambridge University Press.
- Colombo, P., Hellmann, J.R., 2002. Ceramic foams from preceramic polymers. *Materials Research Innovations* 6 (5–6), 260–272.
- Daoush, W., Francis, A., Lin, Y., German, R., 2015. An exploratory investigation on the in-situ synthesis of SiC/AlN/Al composites by spark plasma sintering. *Journal of Alloys and Compounds* 622, 458–462.
- Deming, Y., Xinfang, Y., Jin, P., 1993. Continuous yarn fibre-reinforced aluminium composites prepared by the ultrasonic liquid infiltration method. *Journal of Materials Science Letters* 12 (4), 252–253.
- Deqing, W., Ziyang, S., Hong, G., Lopez, H.F., 2001. Synthesis of lead–fly-ash composites by squeeze infiltration. *Journal of Materials Synthesis and Processing* 9 (5), 247–251.
- Estrada-Guel, I., Carreño-Gallardo, C., Mendoza-Ruiz, D.C., *et al.*, 2009. Graphite nanoparticle dispersion in 7075 aluminum alloy by means of mechanical alloying. *Journal of Alloys and Compounds* 483 (1–2), 173–177. Aug 26.
- Finckenor, M.M., 2017. *Materials for Spacecraft*. Alabama: NASA, Marshall Space Flight Center. Available from: <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160013391.pdf> (Accessed: 11.02.2017).
- Girot, F.A., Albingre, L.O., Quenisset, J.M., Naslain, R.O., 1987. Rheocasting Al matrix composites. *JOM* 39 (11), 18–21.
- Gul, F., Acilar, M., 2004. Effect of the reinforcement volume fraction on the dry sliding wear behaviour of Al–10Si/SiCp composites produced by vacuum infiltration technique. *Composites Science and Technology* 64 (13–14), 1959–1970.
- Gumus, M., 2009. Reducing cold-start emission from internal combustion engines by means of thermal energy storage system. *Applied Thermal Engineering* 29 (4), 652–660.
- Gupta, M., Sharon, N.M.L., 2011. *Magnesium Alloys, and Magnesium Composites*. Hoboken, NJ: John Wiley & Sons.
- Hashim, J., Looney, L., Hashmi, M.S., 1999. Metal matrix composites: Production by the stir casting method. *Journal of Materials Processing Technology* 92, 1–7.
- Jamaati, R., Toroghinejad, M.R., 2010. Manufacturing of high-strength aluminum/alumina composite by accumulative roll bonding. *Materials Science and Engineering A* 527 (16–17), 4146–4151.
- Jayalakshmi, S., Singh, R.A., Gupta, M., 2016. Synthesis of light metal nanocomposites: Challenges and opportunities. *Indian Journal of Advances in Chemical Science* S1, 283–288.
- Kerti, I., Toptan, F., 2008. Microstructural variations in cast B4C-reinforced aluminium matrix composites (AMCs). *Materials Letters* 62 (8–9), 1215–1218.
- Kok, M., 2005. Production and mechanical properties of Al_2O_3 particle-reinforced 2024 aluminium alloy composites. *Journal of Materials Processing Technology* 161 (3), 381–387.
- Lee, K.B., Choi, J.H., Kwon, H., 2009. Characteristic reaction products in the AZ91/SiC composite fabricated by pressureless infiltration technique. *Metals and Materials International* 15 (1), 33–36.
- Li, X., Yang, Y., Cheng, X., 2004. Ultrasonic-assisted fabrication of metal matrix nanocomposites. *Journal of Materials Science* 39 (9), 3211–3212.
- Li, X., Yang, Y., Weiss, D., 2007. Ultrasonic Cavitation Based Dispersion of Nanoparticles in Aluminium Melts for Solidification Processing of Bulk Aluminum Matrix Nanocomposite: Theoretical Study, Fabrication and Characterization. In: *American Foundry Society Transactions*, 133. Schaumburg: American Foundry Society Transactions, pp. 1–2.
- Luo, A., 1995. Processing, microstructure, and mechanical behavior of cast magnesium metal matrix composites. *Metallurgical and Materials Transactions A* 26 (9), 2445–2455.
- Lutsey, N., 2010. Review of Technical Literature and Trends Related to Automobile Mass Reduction Technology. California Air Resources Board., (UCD-ITS-RR-10-10. Available from: <https://escholarship.org/uc/item/9t04t94w>), (Accessed: 25.01.2019)
- Macke, A., Schultz, B.F., Rohatgi, P., 2012. Metal matrix composites. *Advanced Materials & Processes* 170 (3), 19–23.
- Manu, K.S., Raag, L.A., Rajan, T.P., Gupta, M., Pai, B.C., 2016. Liquid metal infiltration processing of metallic composites: A critical review. *Metallurgical and Materials Transactions B* 47 (5), 2799–2819.
- Mavhungu, S.T., Akinlabi, E.T., Onitiri, M.A., Varachia, F.M., 2017. Aluminum matrix composites for industrial use: Advances and trends. *Procedia Manufacturing* 7, 178–182.
- Meyers, M.A., Chawla, K.K., 2008. *Mechanical Behavior of Materials*. Cambridge university press.
- Miracle, D.B., 2005. Metal matrix composites—from science to technological significance. *Composites science and Technology* 65 (15–16), 2526–2540.
- Montanaro, L., Jorand, Y., Fantozzi, G., Negro, A., 1998. Ceramic foams by powder processing. *Journal of the European Ceramic Society* 18 (9), 1339–1350.
- Mortensen, A., 2000. *Comprehensive Composite Materials*, Vol. 3: Metal Matrix Composites. PERGAMON. pp. 521–554.
- Mortensen, A., Jin, I., 1992. Solidification processing of metal matrix composites. *International Materials Reviews* 37 (1), 101–128.
- Nie, J., Li, D., Wang, E., Liu, X., 2014. In-situ synthesis of SiC particles by the structural evolution of TiCx in Al–Si melt. *Journal of Alloys and Compounds* 613, 407–412.
- Nienow, A.W., EDWARDS, M.F., Hamby, N., 1997. *Mixing in the Process Industries*. Butterworth-Heinemann.
- Padhi, P., Kar, S., 2011. A novel route for development of bulk Al/SiC metal matrix nanocomposites. *Journal of Nanotechnology* 2011, Article ID 413512, 5. doi:10.1155/2011/413512.
- Pan, J., Yang, D.M., Wan, H., Yin, X.F., 1995. *Key Engineering Materials* 104–107, 275–282.
- Qi, L.H., Su, L.Z., Zhou, J.M., *et al.*, 2012. Infiltration characteristics of liquid AZ91D alloy into short carbon fiber preform. *Journal of Alloys and Compounds* 527, 10–15.
- Ramanathan, A., Krishnan, P.K., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *Journal of Manufacturing Processes* 42, 213–245.
- Rohatgi, P.K., Ray, S., Liu, Y., 1992. Tribological properties of metal matrix-graphite particle composites. *International Materials Reviews* 37 (1), 129–152.
- Rohatgi, P.K., Tiwari, V., Gupta, N., 2006. Squeeze infiltration processing of nickel coated carbon fiber reinforced Al–2014 composite. *Journal of Materials Science* 41 (21), 7232–7239.
- Rosso, M., 2006. Ceramic and metal matrix composites: Routes and properties. *Journal of Materials Processing Technology* 175 (1–3), 364–375.
- Sahu, P.S., Banchhor, R., 2016. Fabrication methods used to prepare Al metal matrix composites-A. *International Research Journal of Engineering and Technology* 3 (10), 123–132.
- Sasaki, G., Adachi, J., Choi, Y.B., *et al.*, 2005. Fabrication of the aluminum matrix composite by ultrasonic infiltration technique. In: *Zhong, Z.Y., Saka, H., Kim, T.H., et al. (Eds.), Materials Science Forum*, vol. 475. Trans Tech Publications Ltd, pp. 921–924.
- Schmidt, S., Beyer, S., Knabe, H., *et al.*, 2004. Advanced ceramic matrix composite materials for current and future propulsion technology applications. *Acta Astronautica* 55 (3–9), 409–420.
- Sepulveda, P., 1997. Gelcasting foams for porous ceramics. *American Ceramic Society Bulletin* 76 (10), 61–65.
- Singh, L., Singh, B., Saxena, K.K., 2020. Manufacturing techniques for metal matrix composites (MMC): An overview. *Advances in Materials and Processing Technologies* 6 (2), 441–457.
- Suresh, S., Shenbag, N., Moorthi, V., 2012. Aluminium-titanium diboride (Al–TiB₂) metal matrix composites: Challenges and opportunities. *Procedia Engineering* 38, 89–97.

- Wannasin, J., Flemings, M.C., 2005. Fabrication of metal matrix composites by a high-pressure centrifugal infiltration process. *Journal of Materials Processing Technology* 169 (2), 143–149.
- White, J., Hughes, I.R., Willis, T.C., Jordan, R.M., 1987. Metal matrix composites based on aluminium lithium and silicon carbide. *Le Journal de Physique Colloques* 48 (C3), C3–347.
- Withers, G., De Waas Tilakaratna, P., 2005. Performance evaluation of ULTALITE® low cost aluminium metal matrix composite based brake drums. *Transactions Journal of Materials and Manufacturing*. 902–907.
- Xiong, B., Yu, H., Xu, Z., Yan, Q., Cai, C., 2011. Fabrication of SiC particulate reinforced AZ91D composite by vacuum-assisted pressure infiltration technology. *Journal of Alloys and Compounds* 509 (29), L279–L283.
- Yang, J., Chung, D.D., 1989. Casting particulate and fibrous metal-matrix composites by vacuum infiltration of a liquid metal under an inert gas pressure. *Journal of Materials Science* 24 (10), 3605–3612.
- Yang, Y., Lan, J., Li, X., 2004. Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Materials Science and Engineering A* 380 (1–2), 378–383.
- Zawrah, M.F., Aly, M.H., 2006. In situ formation of Al_2O_3 -SiC-mullite from Al-matrix composites. *Ceramics International* 32 (1), 21–28.
- Zweben, C., 2005. Ultrahigh-thermal-conductivity packaging materials. In: *Proceedings of the IEEE Twenty First Annual IEEE Symposium on Semiconductor Thermal Measurement and Management*. pp. 168–174.

Solid Phase Processing of Metal Matrix Composites

Mingyang Zhou, Science and Technology on Reactor System Design Technology Laboratory, Nuclear Power Institute of China, Chengdu, China

Lingbao Ren, Xi'an Jiaotong University, Xi'an, China

Gaofeng Quan, Southwest Jiaotong University, Chengdu, China

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

MMCs exhibit superior mechanical properties, such as higher specific strength and specific elastic modulus than their monolithic counterparts when properly designed and processed (Mortensen and Llorca, 2010). During the past four decades, more and more cost-effective processing and characterization techniques have been developed leading to more frequent applications of MMCs in military, aerospace, electronics, ground transportation and some recreational and infrastructure industries (Miracle, 2005; Zhang *et al.*, 2020). The progressive increase in applications of MMCs has also triggered more research for further advancement in their overall development including processing techniques.

The key points for achieving good mechanical properties of MMCs are the combination of uniform dispersion of reinforcements, good interfacial bonding between metallic matrix and reinforcements, and good structural integrity of reinforcements. To obtain a good combination of these three factors, it is essential to choose an appropriate processing method. In general, according to the different routes of incorporating reinforcements into matrix, the processing methods can be categorized into four types, namely, liquid-state processing, solid-state processing, gaseous-state processing and two-phase processing.

Compared to liquid-state processing methods, the solid-state ones are easier to control to realize uniform reinforcement distribution and homogeneous matrix microstructure (Chawla and Chawla, 2013). In addition, the lower temperatures involved in solid processing can suppress the adverse interfacial reactions between the matrix and reinforcements, which is conducive to obtaining superior mechanical properties. Besides, solid-state processing methods have much lower requirements for equipment, when compared to gaseous-state processing methods, like physical vapor deposition (PVD). Therefore, solid-state processing methods are always important during the whole development process for MMCs, which have been attracting much attention.

The aim of this article is to provide an overview of the progress in solid-state processing methods, including the primary preparation techniques and secondary thermal mechanical processing methods. The novel processing routes developed recently are also described in detail.

Powder Metallurgy

The most common solid-phase processing methods of MMCs are based on powder metallurgy (PM). In fact, it can be employed to fabricate all types of discontinuously reinforced MMCs due to the ease of dispersing discontinuous reinforcements. According to the different methods of adding the reinforcements into the metallic matrix, PM routes can be divided into two types: (1) ex-situ processing route, and (2) in-situ processing route. The ex-situ route usually involves three steps: (1) directly mixing of metal and reinforcement powders to achieve uniform dispersion of reinforcements, (2) consolidation of composite powders, and (3) sintering. In most of these cases, the fully dense compacts are subjected to post-sintering deformation processes, such as hot extrusion, hot forging, hot rolling and severe plastic deformation, which will be described in Section "Thermo-Mechanical Processing (TMP)". For in-situ route, the essential difference is that the reinforcements are generated by in-situ reaction at the initial stage of the processing. All other steps are almost the same as the ex-situ one.

There are several advantages of PM over other preparation routes. The main advantage is that any designed composition of MMCs can be synthesized exactly, because PM is not dictated by thermodynamics and the phase diagram as in the case of liquid metallurgy (Agarwal *et al.*, 2011). In addition, there is little loss of the materials during PM and the final components with intricate shapes can be fabricated, almost with no need for further machining.

Forthcoming section will describe the main stages involved in conventional PM processing in detail, and introduce some new techniques based on PM, which are proposed recently.

Conventional Methods

Dispersion of reinforcements

The dispersion of reinforcements in the composite powders is crucial, which can almost determine the distribution of the reinforcements in the final MMCs, because the following processes, such as compaction and sintering, do not improve the dispersion further. To uniformly disperse the reinforcements in metal matrix, two different methods, namely blending and mechanical alloying, are usually employed. The former method normally involves dry mixing the metallic powders with the desired volume fraction of reinforcements. This method can be used to incorporate reinforcements such as ceramic particulates

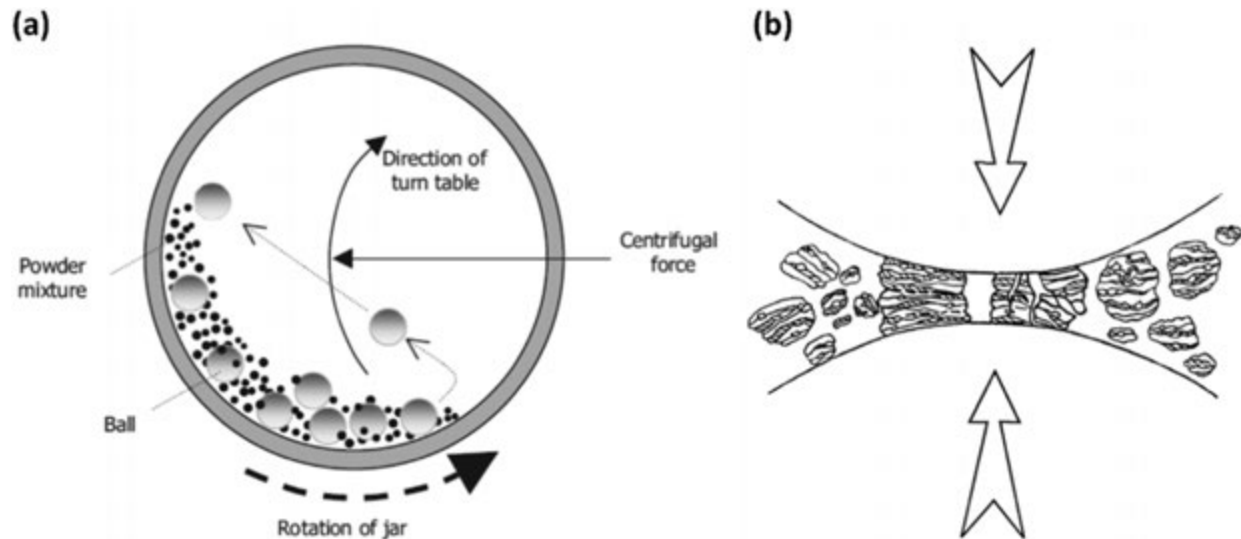


Fig. 1 Schematic diagram showing (a) ball milling process, and (b) ball-powder-ball collision of powder mixture during mechanical alloying. Reproduced from (a) Gupta, M., Sharon, N.M.L., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites*, first ed. New Jersey: John Wiley & Sons. (b) Suryanarayana, C., 2004. *Mechanical Alloying and Milling*, first ed. New York: Marcel Dekker.

and short fibers, into the matrix but the uniformity remains limited (Ibrahim *et al.*, 1991). As for nano reinforcements, particularly, mechanical alloying involving high energy ball milling process is a much better choice. The composite powders undergo high-energy collision during ball-milling as shown in Fig. 1 which is beneficial to disperse the reinforcements and obtain refined grains in metallic matrix (Suryanarayana, 2004). The drawback of the methods is that the high-energy collision will destroy the structural integrity of the reinforcements, especially for the nano carbon materials with special structure, such as carbon nanotubes (CNTs) and graphene nanoplates (GNPs), which will reduce the strengthening effects of these nano reinforcements, resulting in dissatisfactory mechanical performance (Tjong, 2013). The improvement measures for solving this problem will be discussed in Section “Novel Methods”.

Compaction

The compaction stage is important for consolidation of the loose powder to obtain fully dense compacts. According to different pressing routes, commonly used consolidation processes can be categorized into two types: (1) uniaxial pressing, and (2) isostatic pressing.

For uniaxial pressing, the ball-milled or blended composite powders are poured into a metal die cavity, and then apply pressure directly in one single direction. Finally, the powder mixture is compacted into a solid piece and subsequently removed from the die.

For the latter pressing method, the essential difference from the former one is that the pressure is applied from all directions. In addition, the composite powders are filled in a flexible membrane or hermetic container, which creates a pressure barrier between the pressurizing medium and the powder mixture. The pressurizing medium used can be either gas or liquid. This method can achieve uniform compaction pressure throughout the compact, leading to a uniform density distribution in the end composite product. However, due to its higher cost and slower processing speed, it is only employed to prepare small quantities and simple shaped materials (Gupta and Sharon, 2011).

Hot pressing can be conducted for both of the two methods by applying pressure and heating simultaneously. Once hot compaction or hot isostatic pressing is utilized, the sintering step is often not required.

Sintering techniques

Sintering process determines the interface bonding between the powders and has a significant effect on the relative density of the final product. The heating temperature is always traditionally below the material's (metallic matrix) melting point. Fig. 2 shows the schematic diagram of different sintering stages. It can be seen that necks are formed along the powder contacts at the initial sintering stage, and the voids also are formed during this stage. As the sintering process progresses, the voids gradually diminish in size, resulting in a denser compact. However, it is hard to produce the compact without any void, thus, the relative density of the MMCs fabricated by PM is usually less than 100%.

For conventional method, the heat for sintering is generated by external sources such as a resistive heating element. The powder mixture is heated through conduction, convection, and radiation. The weak point of conventional sintering is that high temperature and long sintering time should be used to obtain dense products with good interfacial bonding (Tjong, 2013). However, this will lead to grain growth of the metallic matrix, which may result in decrease in strength of the MMCs. In order to reduce the adverse effects of the heating process, researchers have developed some novel sintering methods, like spark plasma sintering (SPS) and microwave sintering.

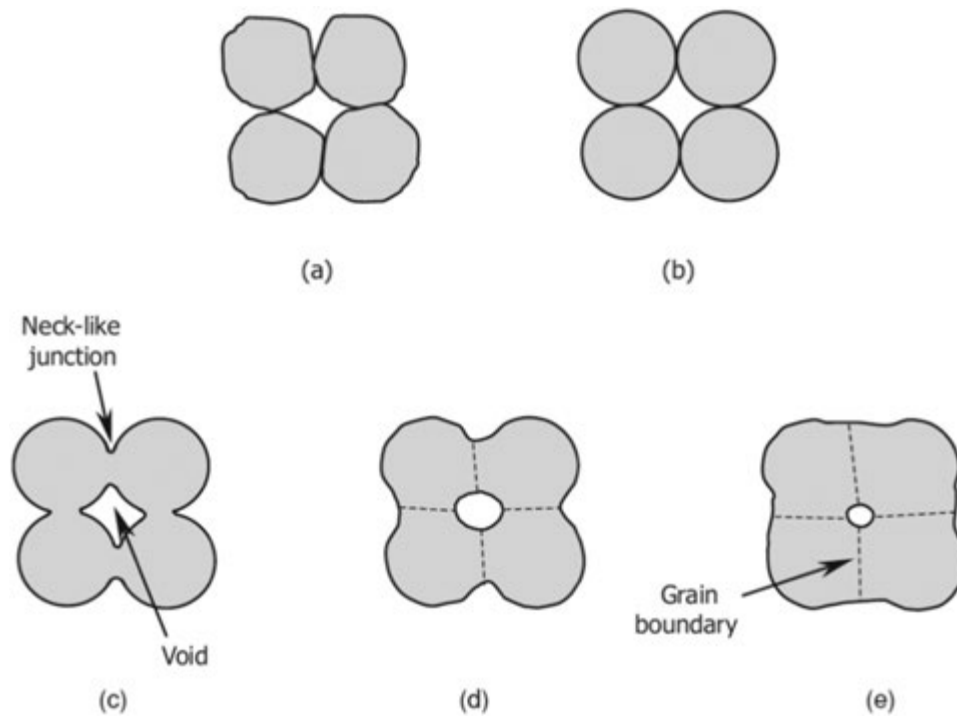


Fig. 2 Schematic diagram showing the sintering stages. Reproduced from Gupta, M., Sharon, N.M.L., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites*, first ed. New Jersey: John Wiley & Sons.

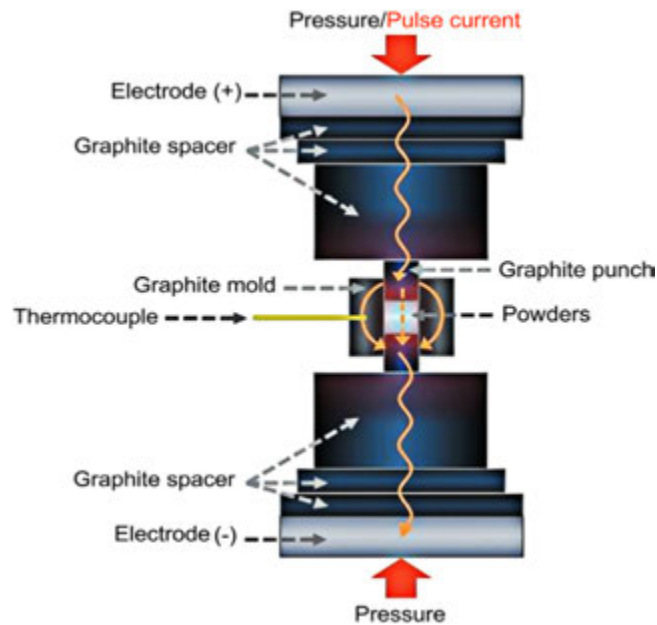


Fig. 3 A schematic view of the SPS apparatus and its components. Reproduced from Azarniya, A., Azarniya, A., Sovizi, S., *et al.*, 2017. Physicomechanical properties of spark plasma sintered carbon nanotube-reinforced metal matrix nanocomposites. *Progress in Materials Science* 90, 276–324.

Spark plasma sintering

SPS is a typical field assisted sintering technique, which can achieve fully dense compacts by using low processing temperature and short sintering time. Thus, it has attracted more and more attentions for fabricating MMCs, especially for MMCs with nano grains (Azarniya *et al.*, 2017). Fig. 3 shows the schematic of the SPS process. In this technique, the direct current (DC) pulse discharge could generate spark plasma, Joule heating, and an effective electrical field diffusion effect. In addition, the application of pressure

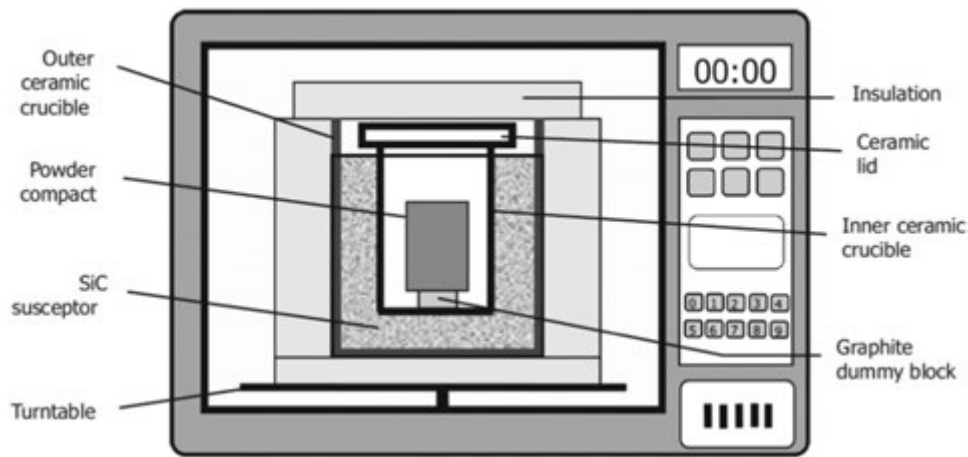


Fig. 4 Schematic diagram of the hybrid microwave heating experimental setup used. Reproduced from Gupta, M., Sharon, N.M.L., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites*, first ed. New Jersey: John Wiley & Sons.

can further promote the consolidation of the materials. Therefore, the nanostructure features of MMCs obtained from ball milling can be preserved by preventing or at least minimizing grain growth through careful control of the SPS parameters, which is promising to achieve superior mechanical properties. Nowadays, SPS has been employed to fabricate a large number of MMCs, and the metallic matrices include Cu, Al, Ag, Ni, Ti, Mg, and Ni (Azarniya *et al.*, 2017).

Microwave sintering

Another novel method is microwave sintering. Heat is generated from within the materials and radiates to the outer surface due to the penetrative power of microwaves. Thus, the temperature of the core of the materials is higher than that of the surface during pure microwave heating. Accordingly, the resulted surface of the MMCs might be relatively poor. In order to overcome the shortcomings of either conventional heating or pure microwave heating, Gupta's research group developed a microwave assisted hybrid sintering technique (Gupta and Wong, 2015), and the hybrid heating experimental setup is as shown in Fig. 4. This method involves a pre-calibrated temperature exposure near the melting point of the metallic matrix in a microwave oven using SiC as the microwave susceptor material. This can provide a more uniform temperature gradient within the billet. In addition, this technique can reduce more than 80% in the sintering time and energy consumption when compared to conventional sintering while realizing higher mechanical properties of the composites. An important difference between the various sintering techniques is that hybrid microwave sintering can be carried out in air without any inert protective atmosphere, while conventional sintering should be conducted in an Ar atmosphere to minimize oxidation. It is worth noting that the end mechanical performance of the hybrid microwave sintered MMCs are not compromised when compared to their conventionally sintered counterparts (Gupta and Wong, 2005). Therefore, this hybrid sintering method is economically viable for industries and is friendly to environment (Wai *et al.*, 2010).

Novel Methods

As mentioned above, both of blending and high energy ball milling in conventional PM have their limitations. The former one is hard to disperse nano reinforcements, while the latter dispersing method will damage the structural integrity of the nano carbon materials. Therefore, more and more attentions have been focused to develop some novel methods, which can uniformly disperse nano reinforcements in metallic matrix and effectively maintain their structural integrity, mainly for CNTs and GNPs. Following sub-sections will systematically introduce some useful techniques which are based on PM, including: (1) semi-powder metallurgy, (2) flake powder metallurgy, (3) molecular level mixing, and (4) in-situ synthesis.

Semi-powder metallurgy

Semi-powder metallurgy involves blending reinforcements and metal powders in slurry, where mechanical stirring and ultrasonication are usually used, and then the powder mixture of the MMC can be obtained after drying in a vacuum drying oven. Subsequent steps are always the same as conventional PM and thus this technique is called semi-PM. Its schematic diagram is shown in Fig. 5. This method can achieve uniform dispersion of CNTs and/or GNPs, which are difficult to disperse by blending, due to the significant effect of ultrasonication. Better results can be obtained, when dispersants for CNTs or GNPs are employed. In addition, the special structure of CNTs or GNPs is perfectly maintained during dispersion process, resulting in an excellent strengthening efficiency.

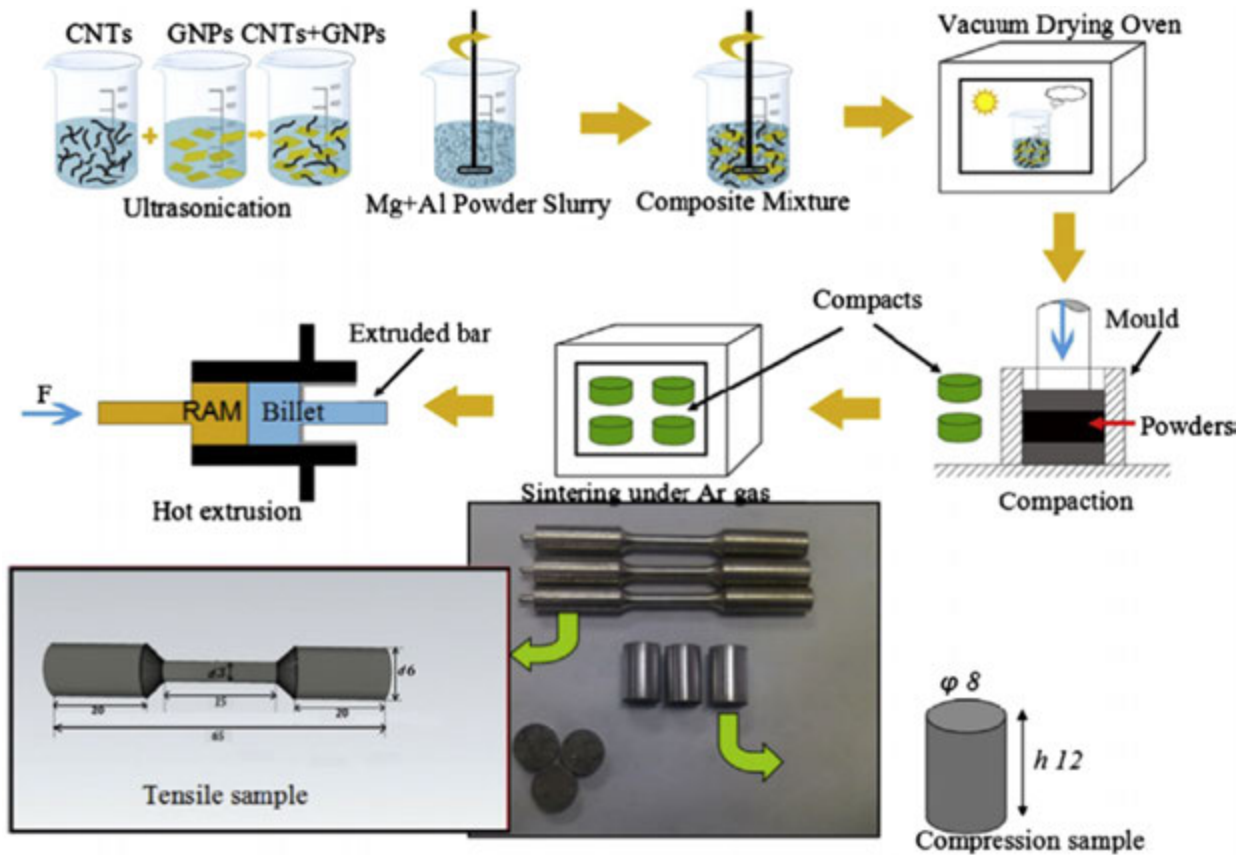


Fig. 5 Schematic of semi powder metallurgy method. Reproduced from Rashad, M., Pan, F.S., Tanga, A., *et al.*, 2014. Synergetic effect of graphene nanoplatelets (GNPs) and multi-walled carbon nanotube (MW-CNTs) on mechanical properties of pure magnesium. *Journal of Alloys and Compounds* 603, 111–118.

Flake powder metallurgy

Another novel method is flake powder metallurgy. As indicated earlier, the severe impact of balls can damage the structural integrity of CNTs or GNPs during the long-time high energy ball milling process which ultimately affects the mechanical properties. To solve this problem, [Xu *et al.* \(2017\)](#) proposed a novel flake powder metallurgy via shift-speed ball milling (SSBM), namely, the combination of long-time low speed ball milling (LSBM) and short-time high speed ball milling (HSBM). The collision force in planetary ball mill could be divided into two types: (1) radial component of compressing force, and (2) tangential component of shearing force ([Cundall and Strack, 1979](#); [Dallimore and McCormick, 1996](#); [Chattopadhyay *et al.*, 2001](#)). The former one mainly contributes to powder deformation such as flattening, cold-welding and fragmenting, while the latter one can effectively disperse the nano reinforcements ([Suryanarayana, 2001](#); [Andrews *et al.*, 2002](#)). To note that both compressing force and shearing force would increase notably as the milling speed increases, leading to significant increase in collision force, which determined the co-deformation and dispersion mechanisms of composite powder mixtures. During LSBM, the mild compressing force would take a long time for the spherical Al powders to become flakes, thus, the shearing force can have enough time to gradually break up the big clusters of CNTs or GNPs and achieve uniform distribution of them on the surface of metal flakes. In HSBM stage, the significantly increased collision force would accelerate the powder flattening and cold welding, which can promote the interfacial bonding between metal powders ([Fig. 6\(a\)](#)). Besides, the damage of the structural integrity of CNTs and GNPs can be acceptable due to the low collision force during LSBM and short period during HSBM. This method has been employed to fabricate Al matrix composites containing CNTs ([Xu *et al.*, 2017](#)) and GNPs ([Jiang *et al.*, 2018](#)), respectively. [Fig. 6\(b\)–\(d\)](#) show the TEM images of the uniform dispersion and structural integrity of CNTs in Al matrix, and the results of mechanical properties compared to other works also revealed that the CNT/Al matrix composites by this SSBM flake PM method has balanced strength and ductility.

[Jiang *et al.* \(2011, 2012\)](#) proposed another new flake PM method. The processing steps of this method are shown in [Fig. 7\(a\)](#). Firstly, nanoflakes of Al were prepared by using high speed ball milling, and then the Al nanoflakes were modified by polyvinyl alcohol (PVA), which can be decorated with hydroxyl groups ($-OH$). The CNTs functionalized with carboxyl groups ($-COOH$) were dispersed in sodium dodecyl benzene sulfonate (SDBS) solution, and then the PVA-modified Al nanoflakes were added into the CNTs suspension. After blending in the slurry, the CNTs were adsorbed onto the surfaces of Al nanoflakes through hydrogen bonding between $-COOH$ groups and $-OH$ groups, resulting in a uniform dispersion of CNTs on the surfaces of Al powders with

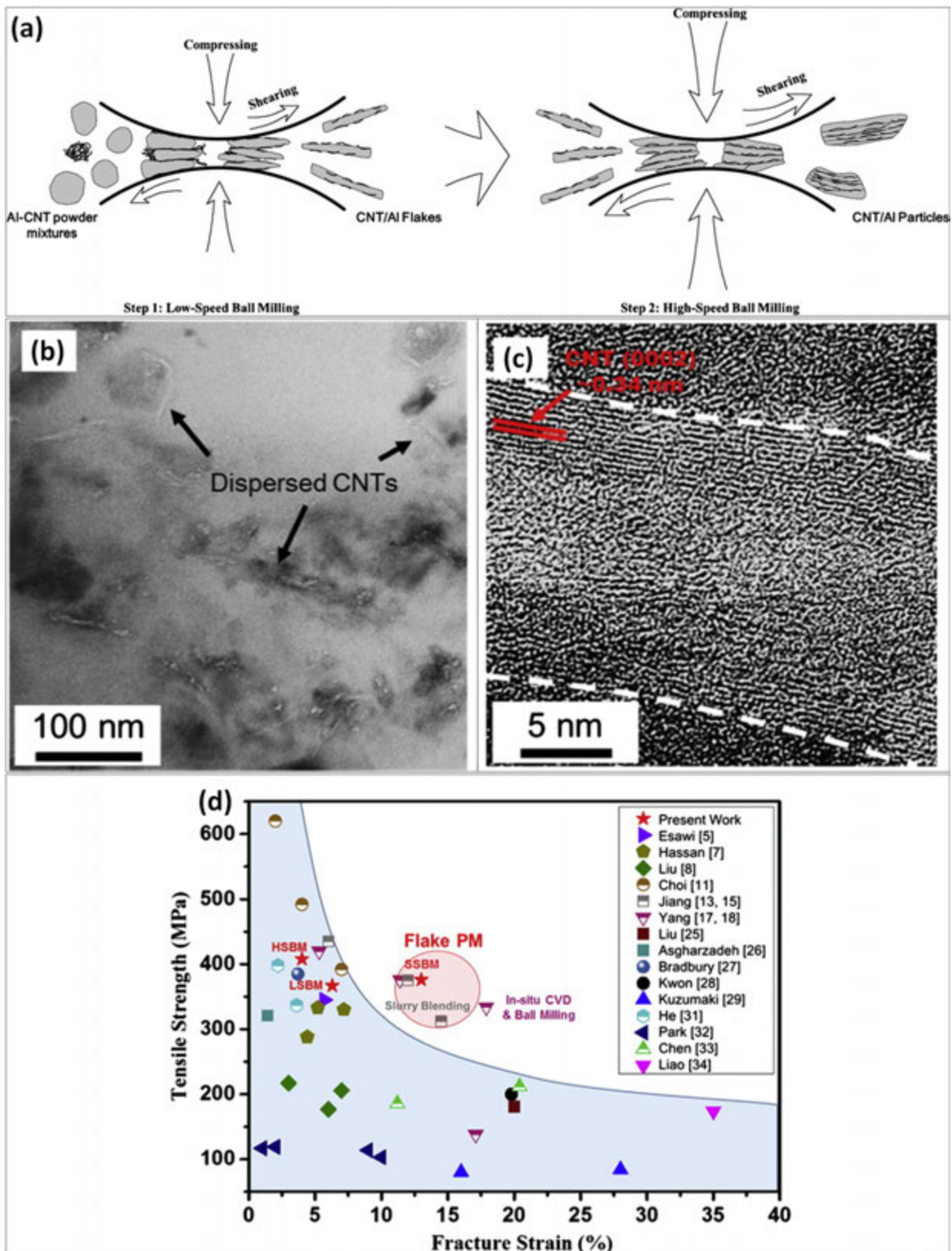


Fig. 6 (a) Illustration of co-deformation/dispersion mechanisms of CNT/Al powders during SSBM, (b) TEM image of SSBM CNT/Al, (c) HRTEM image of an individual CNT in (b), and (d) representative tensile properties of PM CNT/Al composites. Reproduced from Xu, R., Tan, Z.Q., Xiong, D.B., *et al.*, 2017. Balanced strength and ductility in CNT/Al composites achieved by flake powder metallurgy via shift-speed ball milling. *Composites Part A: Applied Science and Manufacturing* 96, 57–66.

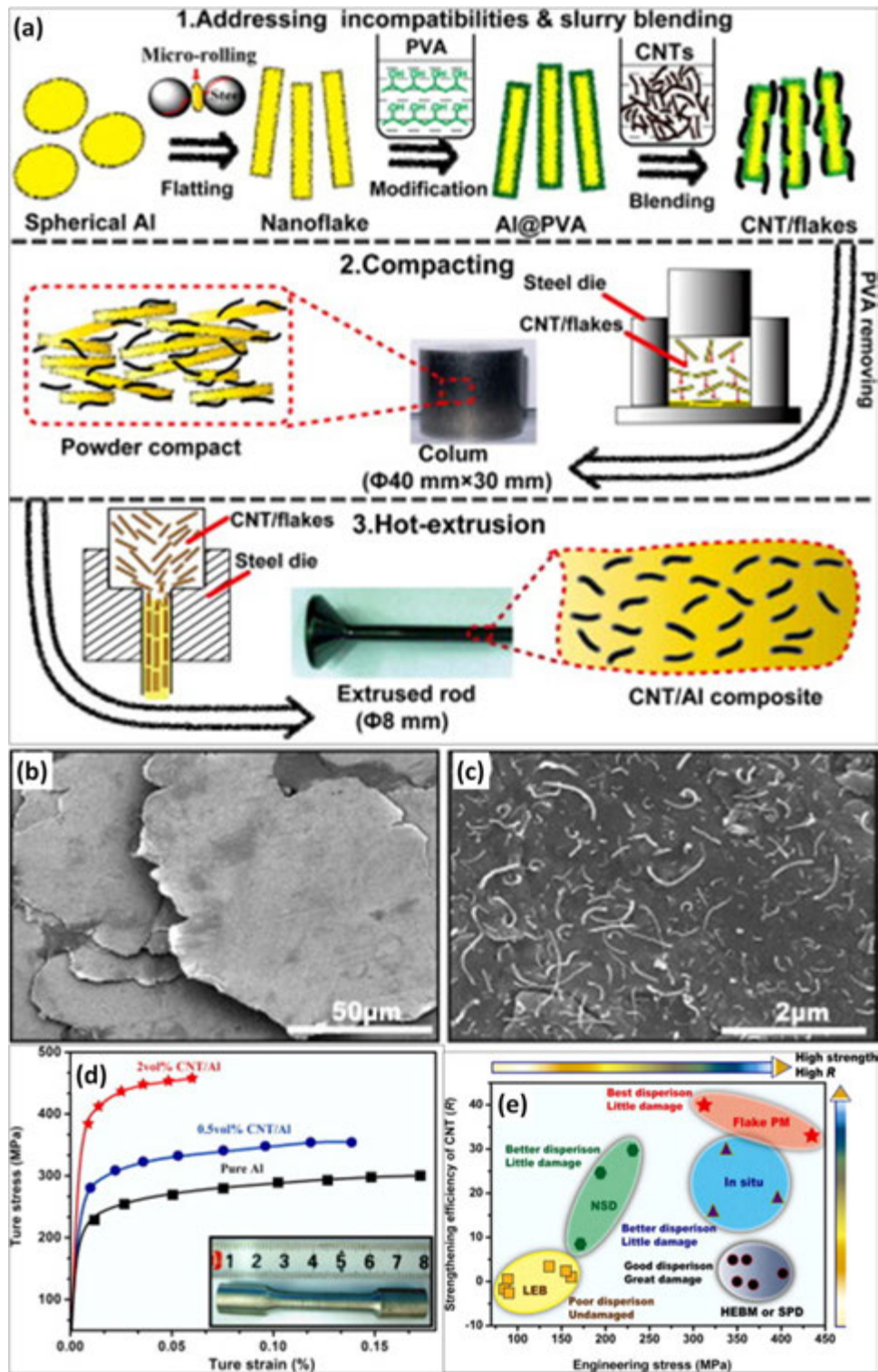


Fig. 7 (a) Illustration of flake PM solution for the uniform dispersion of CNTs in Al matrix, (b) and (c) FE-SEM of Al flake powder without and with CNTs, respectively, (d) Tensile performance of CNT/Al composites achieved by flake PM, and (e) the strengthening efficiency and tensile strength for CNT/Al composites fabricated by various methods. Reproduced from Jiang, L., Fan, G.L., Li, Z.Q., *et al.*, 2011. An approach to the uniform dispersion of a high volume fraction of carbon nanotubes in aluminum powder. *Carbon* 49 (6), 1965–1971. Jiang, L., Li, Z.Q., Fan, G.L., Cao, L.L., Zhang, D., 2012. The use of flake powder metallurgy to produce carbon nanotube (CNT)/aluminum composites with a homogenous CNT distribution. *Carbon* 50 (5), 1993–1998.

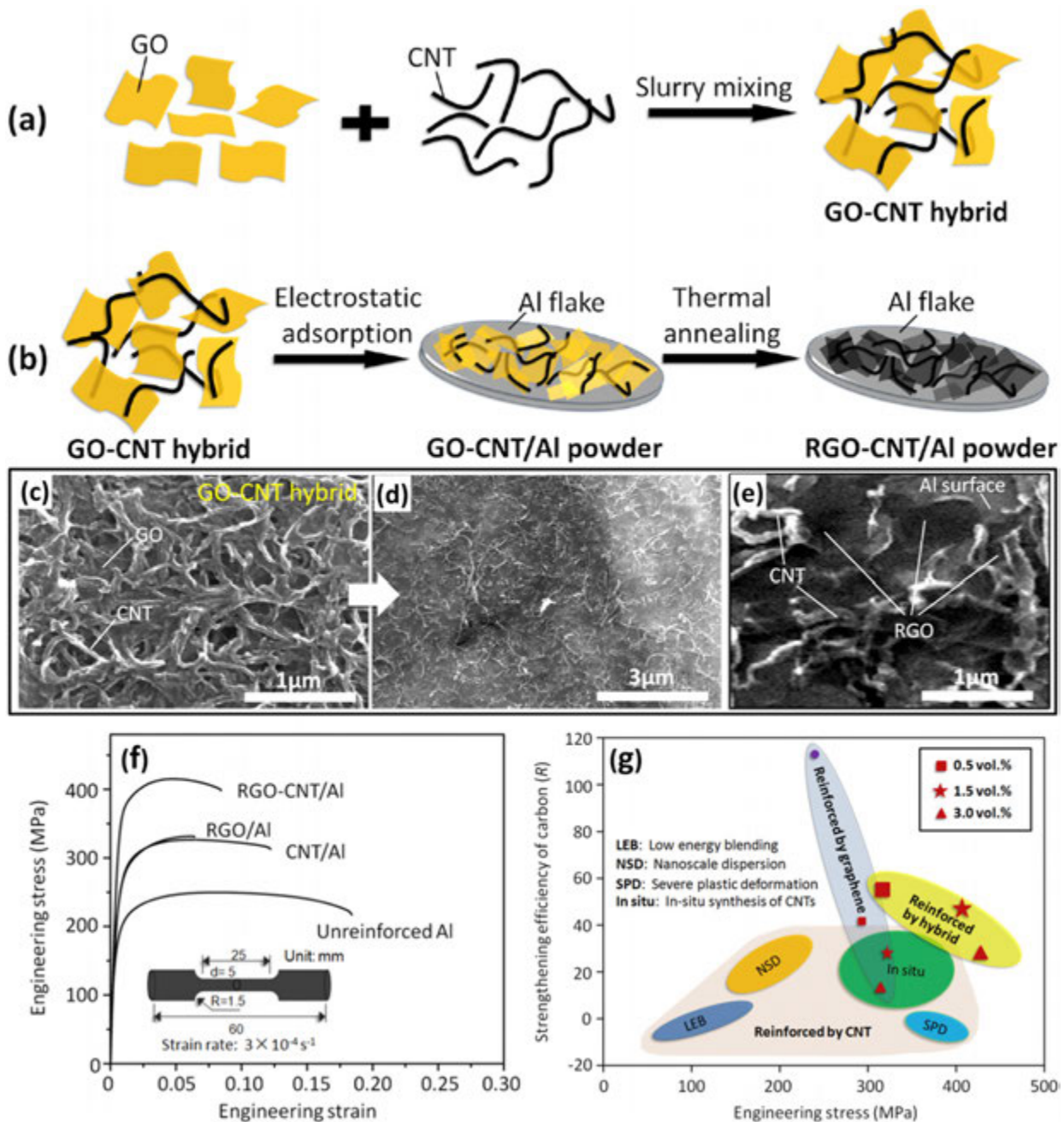


Fig. 8 Illustration of the fabrication procedure of RGO-CNT/Al composite powders. (a) The spontaneous formation of GO-CNT hybrid through π - π interactions, (b) Electrostatic adsorption of GO-CNT hybrid on Al flake and the reduction of GO to RGO through thermal annealing; (c) SEM image of the GO-CNT hybrid before being adsorbed on Al flakes, (d) SEM image of the composite powders reinforced by GO-CNT hybrid after adsorption and annealing process, and (e) the magnified rendition of the composite flake surface of (d); (f) Stress-strain curves of Al and composites reinforced by 1.5 vol% of the hybrid, individual RGO, and individual CNT, Comparison of the tensile strength and strengthening efficiency of carbon in RGO-CNT/Al composite with the reported CNT- and graphene-reinforced Al matrix composite systems. Reproduced from Li, Z., Fan, G.L., Guo, Q., *et al.*, 2015. Synergistic strengthening effect of graphene-carbon nanotube hybrid structure in aluminium matrix composites. Carbon 95, 419–427.

very little structure damage (Fig. 7(c)). The composite powders were then obtained by vacuum drying and heating in a flowing Ar atmosphere at high temperature to remove the PVA. The subsequent steps remain similar to that of conventional PM. Finally, the high strength and remarkable strengthening efficiency (Fig. 7(d) and (e)) were mainly attributed to the homogeneous and individual distribution of CNTs in Al matrix and their retained structural integrity.

Li *et al.* (2015) developed a similar and improved flake PM method (as shown in Fig. 8(a) and (b)). The main difference is that dispersion of hybrid CNTs and RGO were assisted by electrostatic adsorption rather than hydrogen bonding. Uniform dispersion

and the maintained structural integrity of hybrid CNTs and RGO were also both obtained (Fig. 8(c)–(e)). Thus, high mechanical performance and strengthening efficiency were achieved (Fig. 8(f) and (g)). It is worth noting that a planar RGO-CNTs network architecture in the composites was formed due to π - π interaction, leading to a significantly higher strengthening efficiency of hybrid GNPs-CNTs than those of individual RGO or CNT reinforcement. The similar technique has also been used to fabricate graphene reinforced Cu matrix composite with high performance (Yang *et al.*, 2018; Yang *et al.*, 2017).

For magnesium alloy matrix composites, the flake powder metallurgy method may be inappropriate due to the strong chemical activity of Mg as it could be severely oxidized during the slurry blending and electrostatic adsorption process (Xiang *et al.*, 2019a,b). Thus, Zhou *et al.* (2019) made some improvements on the basis of the methods mentioned above and developed another PM route which is efficient and suitable for Mg matrix to prepare multi-scale hybrid micron SiC and CNTs reinforced Mg matrix composites (Fig. 9(a)). This route involves a multi-step dispersion process. First, the CNTs were uniformly adsorbed onto the surface of the SiC (Fig. 9(b) and (c)) through hydrogen bonding between the carboxyl (–COOH) groups and hydroxyl (–OH) groups, which were decorated on the surfaces of the CNTs and SiC, respectively. Then, shift-speed ball milling was employed to achieve a uniform dispersion of the hybrid reinforcements in the end composites. In this route, the micron SiC particles can act as carrier to transfer the CNTs from the surface of the SiC into the matrix. Because micron size SiC particles can be easily dispersed in metallic matrix uniformly via ball milling, the ball milling time needed to disperse CNTs uniformly in the matrix can be much shorter than common ball milling methods. Therefore, this route can significantly improve the dispersion efficiency of the CNTs in the matrix. In addition, the shorter ball milling time can also contribute in maintaining the structural integrity of CNTs. By ensuring structural integrity of reinforcement and uniform dispersion of multi-scale hybrid reinforcements in the Mg matrix (Fig. 9(e)–(g)), good combination of ultra-high strength and good ductility was successfully achieved (Fig. 9(h)).

Molecular level mixing

Molecular level mixing is a composite powder preparation technique, especially for composite containing CNTs or GNPs, and as the name suggests, the dispersion of the nano reinforcements is achieved on the molecular level by using this technique (Bakshi *et al.*, 2010). Fig. 10 shows the schematic of molecular-level mixing process for preparing Cu-CNT composite powders. The method involves acid treatment and functionalization of the CNTs before introducing them into copper salt ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) solution, which can promote the CNT suspension and surface metal deposition on their surface. The treated CNTs are then added into the Cu salt bath and dispersed by using ultrasonication to prepare the CNT-Cu ion precursor. Subsequently, the precursor would undergo drying, calcinations and a reduction process to produce Cu-CNT composite powders. It is worth noting that the reduction process can also be conducted by using reducing agents directly in the bath to shorten the preparation time (Xu *et al.*, 2007). Finally, conventional PM route are always employed to fabricate bulk MMCs for these nanocomposite powders prepared by molecular-level mixing technique. In addition to Cu-CNT system, Chen *et al.* (2003) synthesized Sb/SbSn0.5-CNT nanocomposite for anode materials in Li-ion batteries. The formation of a semi-continuous layer of metal on CNTs was reported by these authors.

The advantage of molecular-level mixing technique is that it has great potential to improve dispersion and interfacial bonding strength of the nano-reinforcements such as CNTs and GNPs with metal matrix, as well as, maintaining the structural integrity of these reinforcements. However, this method can only be applied to metallic matrix with weak reducibility like Cu, and Au and thus there are only a few studies of this method reported until now.

In-situ synthesis

In-situ methods involves synthesis of MMCs in which the reinforcements are generated in a metallic matrix by using chemical reactions between elements or between elements and compounds during the fabrication process of the composites (Tjong and Ma, 2000). Moreover, compared to the MMCs fabricated by using ex-situ processing techniques, the in-situ MMCs have three main merits (Tjong and Ma, 2000): (1) the reinforcements formed by in-situ reactions are thermodynamically stable in the metallic matrix, which can be employed in elevated-temperature services, (2) a good interfacial bonding can be achieved due to the clean interface between in-situ reinforcements and metallic matrix and (3) the in-situ formed reinforcements are always fine in size and distribute more homogeneously in metallic matrix when compared to ex-situ reinforcements. Therefore, the in-situ MMCs exhibit superior room and elevated temperature mechanical performance due to the above-mentioned advantages and hence have the great potential for widespread applications. Thus, more and more attention has been paid to develop new techniques and optimizing processing parameters for in-situ methods during the past decades. According to the different types of in-situ reinforcements, we categorized two groups of in-situ techniques: (1) in-situ ceramic phases, and (2) in-situ carbonaceous materials.

For in-situ ceramic phases, a number of reactive systems have been investigated during the past three decades. And Al, Ti, C and B are four most frequently used elements. There are six typical reactive systems, namely, Al-Ti-C, Al-Ti-B, Ti-C, Ti-B₄C, Ti-TiB₂, and molten salt systems. These are summarized in Table 1. For PM route, the first five systems are often used. Ball milling is usually utilized to disperse the reactants or compounds uniformly onto the surfaces of metallic matrix powders. In this step, in order to avoid severe plastic deformation and oxidation, the appropriate parameters of ball milling should be employed (Wei *et al.*, 2018). The milled mixtures are subsequently compacted or hot-pressed and sintered at optimized parameters obtained via thermodynamic and kinetic calculations as well as experimental verifications. Ma *et al.* (1996) fabricated in-situ hybrid Al₂O₃ and TiB₂ particulates reinforced Al matrix composites with superior mechanical properties by using powder metallurgy technique. High

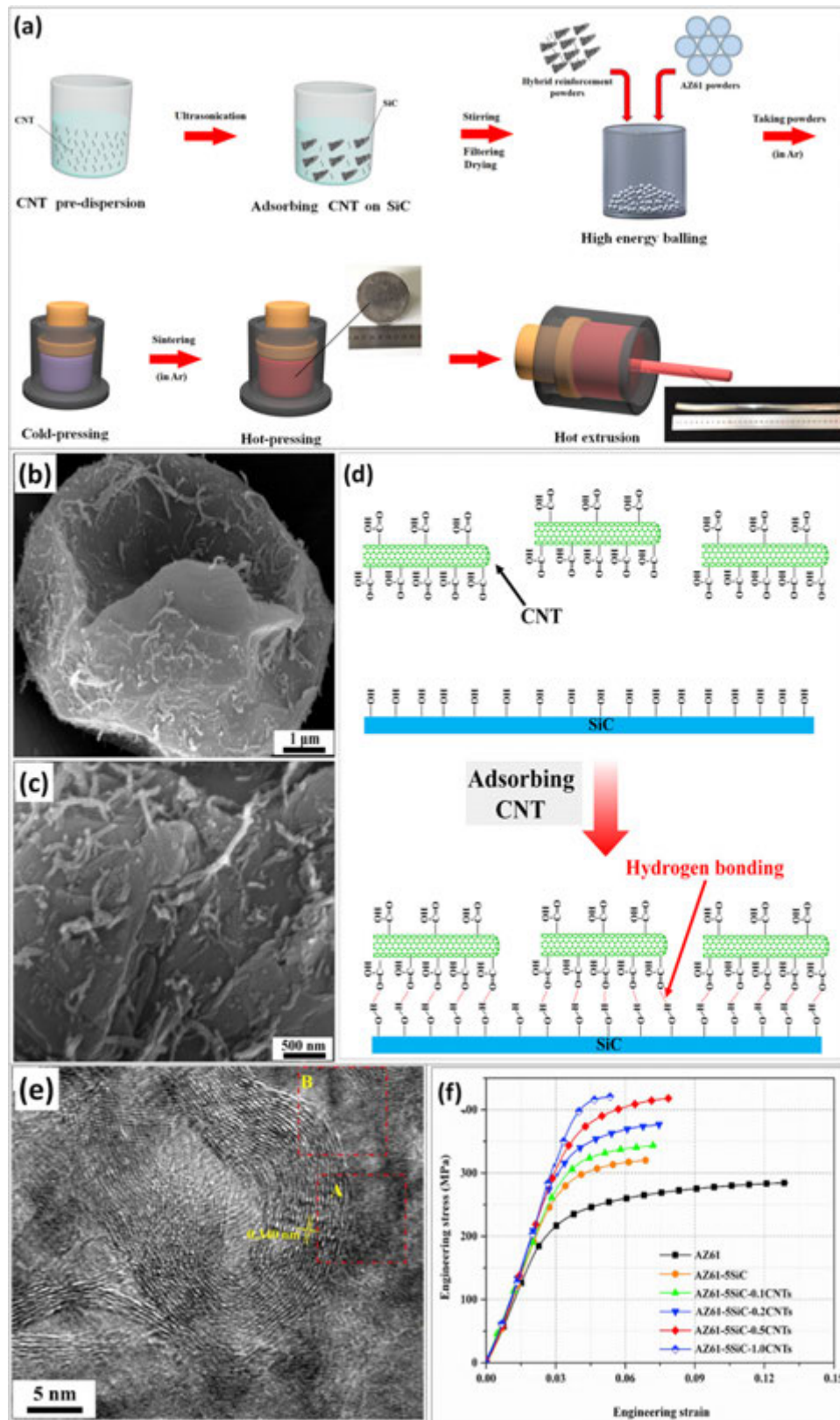


Fig. 9 (a) Schematic illustration of the fabrication process of multi-scale hybrid micron SiC and CNTs reinforced AZ61 alloy composites, (b) and (c) SEM images of the CNTs adsorbed on SiC surface, (d) schematic of adsorption of CNTs onto the surface of SiC, (e) HRTEM image showing interfacial microstructure in AZ61-5SiC-0.5 CNTs composite, (f) (g) partial enlargement at selection region (A and B, respectively), and (h) engineering tensile stress-strain curves of AZ61 and its composites. Reproduced from Zhou, M.Y., Ren, L.B., Fan, L.L., *et al.*, 2019. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. *Materials Science and Engineering A* 768 (19), 138447.

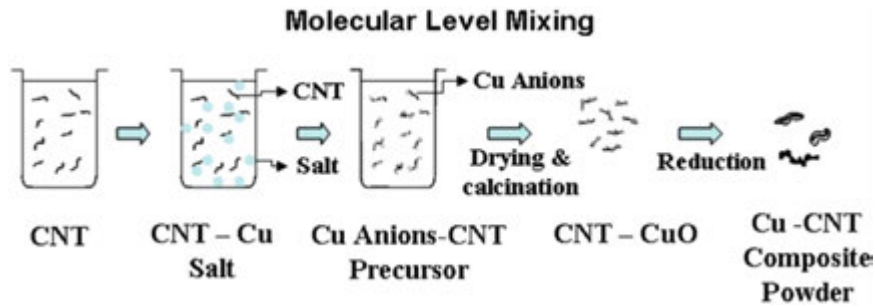


Fig. 10 Schematic of molecular-level mixing process. Reproduced from Bakshi, S.R., Lahiri, D., Agarwal, A., 2010. Carbon nanotube reinforced metal matrix composites – A review. *International Materials Reviews* 55 (1), 41–64.

Table 1 Reaction systems of in-situ developed ceramic phases

Reaction systems	Reaction equations
Al-Ti-C system	$\text{Ti} + \text{C} \rightarrow \text{TiC}$ $4\text{Al} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3$ $\text{Ti} + 3\text{Al} \rightarrow \text{Al}_3\text{Ti}$ $3\text{Al}_3\text{Ti} + \text{Al}_4\text{C}_3 \rightarrow 3\text{TiC} + 13\text{Al}$ $\text{Al}_3\text{Ti} + \text{C} \rightarrow \text{TiC} + 3\text{Al}$
Al-Ti-B system	$\text{Al} + 2\text{B} \rightarrow \text{AlB}_2$ $\text{Ti} + 3\text{Al} \rightarrow \text{Al}_3\text{Ti}$ $\text{Al}_3\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2 + 3\text{Al}$ $\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2$ $\text{Ti} + 3\text{Al} \rightarrow \text{Al}_3\text{Ti}$ $2\text{H}_3\text{BO}_3 + 3\text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{AlB}_2 + 3\text{H}_2\text{O}$ $\text{Al}_3\text{Ti} + \text{AlB}_2 \rightarrow \text{TiB}_2 + 4\text{Al}$ $\text{Al} + 2\text{B} \rightarrow \text{AlB}_2$ $6\text{TiO}_2 + 2\text{Al} \rightarrow 3\text{Ti}_2\text{O}_3 + \gamma - \text{Al}_2\text{O}_3$ $\text{Ti}_2\text{O}_3 + 2\text{AlB}_2 \rightarrow 2\text{TiB}_2 + \alpha - \text{Al}_2\text{O}_3$ $3\text{AlB}_2 + 3\text{TiO}_2 + \text{Al} \rightarrow 3\text{TiB}_2 + 2\alpha - \text{Al}_2\text{O}_3$ $3\text{TiO}_2 + 13\text{Al} \rightarrow 3\text{Al}_3\text{Ti} + 2\alpha - \text{Al}_2\text{O}_3$ $\text{AlB}_2 + \text{Al}_3\text{Ti} \rightarrow \text{TiB}_2 + 4\text{Al}$
Ti-C system	$\text{Ti} + \text{C} \rightarrow \text{TiC}$
Ti-B ₄ C system	$5\text{Ti} + \text{B}_4\text{C} \rightarrow 4\text{TiB} + \text{TiC}$ $3\text{Ti} + \text{B}_4\text{C} \rightarrow 2\text{TiB}_2 + \text{TiC}$
Ti-TiB ₂ system	$\text{TiB}_2 + \text{Ti} \rightarrow 2\text{TiB}$
Ti-SiC system	$3\text{Ti} + 2\text{SiC} \rightarrow \text{Ti}_3\text{SiC}_2 + \text{Si}$ $\text{Ti} + \text{SiC} \rightarrow \text{Si} + \text{TiC}$ $3\text{Si} + 5\text{Ti} \rightarrow \text{Ti}_5\text{Si}_3$
Molten salt system	$2\text{TiO}_2 + 2\text{Na}_3\text{AlF}_6 \rightarrow 2\text{Na}_2\text{TiF}_6 + \text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ $2\text{Na}_2\text{TiF}_6 + 6\text{Al} \rightarrow 4\text{NaF} + 4\text{F}_2 + 2\text{TiAl}_3$ $\text{Al}_2\text{O}_3 + 2\text{Na}_3\text{AlF}_6 \rightarrow 4\text{Na}_2\text{O} + 4\text{Al} + 6\text{F}_2$ $2\text{Na}_2\text{TiF}_6 + 4\text{Al} + \text{KBF}_4 \rightarrow \text{TiAl}_3 + \text{TiB}$ $+ 4\text{NaF} + \text{AlF}_3 + \text{KF} + 4\text{F}_2$ $2\text{Na}_2\text{TiF}_6 + 3\text{Al} + 2\text{KBF}_4 \rightarrow \text{TiAl}_3 + \text{TiB}_2$ $+ 4\text{NaF} + 2\text{KF} + 7\text{F}_2$ $\text{Na}_2\text{TiF}_6 + \text{KBF}_4 \rightarrow \text{TiB} + 2\text{NaF} + \text{KF} + 4\text{F}_2$

Note: Zhou, M.Y., Ren, L.B., Fan, L.L., *et al.*, 2020. Progress in research on hybrid metal matrix composites. *Journal of Alloys and Compounds* 838, 155274.

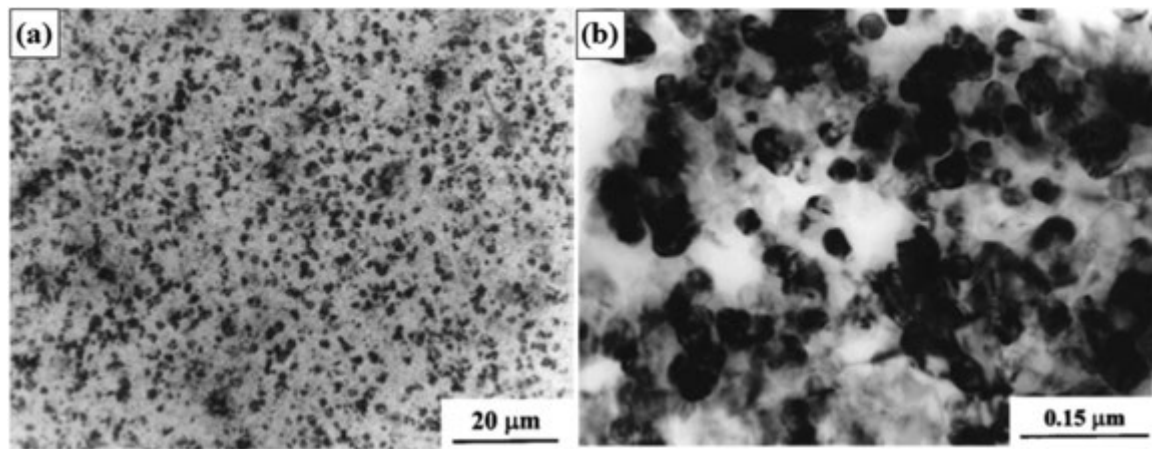


Fig. 11 (a) Optical micrograph showing uniform distribution of fine Al₂O₃ and TiB₂ particulates in aluminum matrix, (b) TEM micrograph showing fine Al₂O₃ and TiB₂ particulates and clean interfaces. Reproduced from Tjong, S.C., Ma, Z.Y., 2000. Microstructural and mechanical characteristics of in situ metal matrix composites. *Materials Science and Engineering R* 29 (3), 49–113.

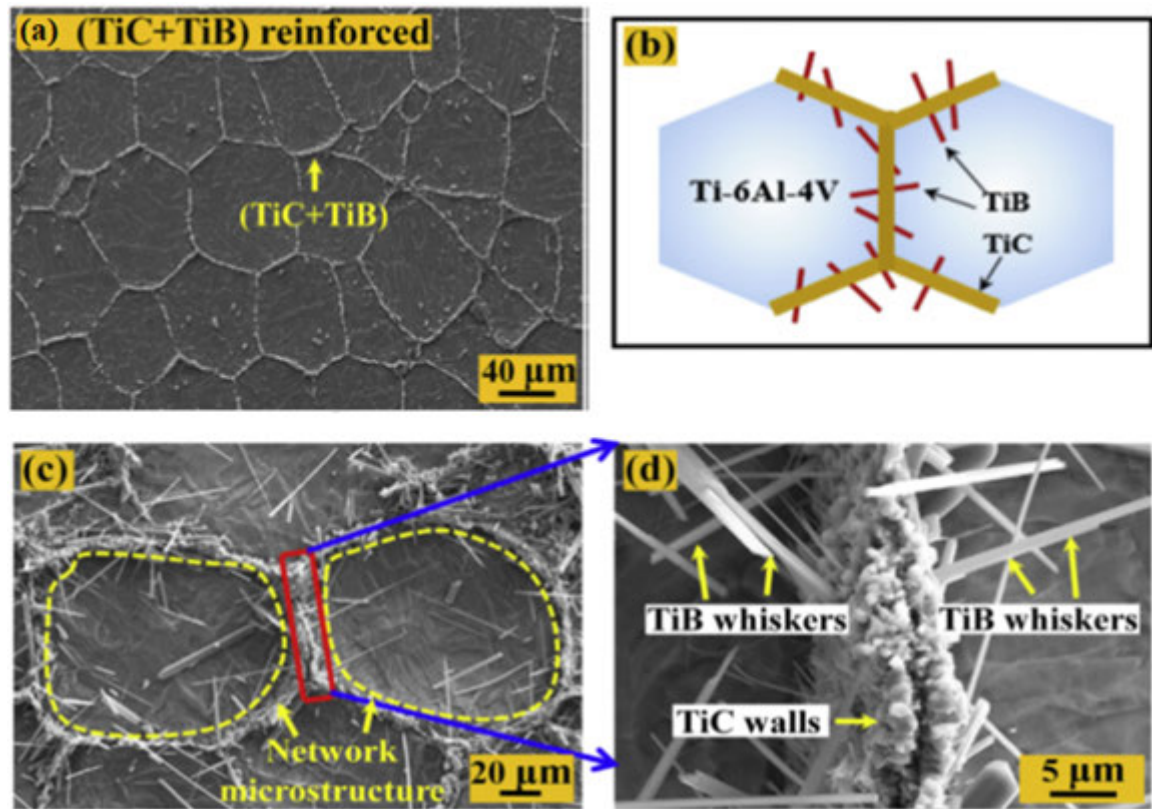


Fig. 12 (a) SEM image of Ti-6Al-4V/(TiC + TiB), (b) schematic of microstructural design, (c) microstructure after deep etching, (d) magnified network microstructure. Reproduced from (d) Wei, S.L., Huang, L.J., Li, X.T., An, Q., Geng, L., 2018. Interactive effects of cyclic oxidation and structural evolution for Ti-6Al-4V/(TiC + TiB) alloy composites at elevated temperatures. *Journal of Alloys and Compounds* 752 (5), 164–178.

performance of the composite was attributed to the uniform distribution of the fine and equiaxed in-situ Al₂O₃ and TiB₂ particulates in Al matrix (Fig. 11(a)) and the clean interfaces between the in-situ reinforcements and Al matrix (Fig. 11(b)).

For Ti matrix composites, the network structures could be formed by in-situ reaction during hot pressing. Wei *et al.* (2018) reported that the in-situ powder metallurgy method can be conducted to prepare hybrid in-situ Ti alloy matrix composites with enhanced high-temperature oxidation resistance due to formation of hybrid (TiC particles + TiB whiskers) networks (as shown in Fig. 12). Even a tailored two-scale architecture can also be achieved in Ti6Al4V composites (Liu *et al.*, 2015). The microstructure

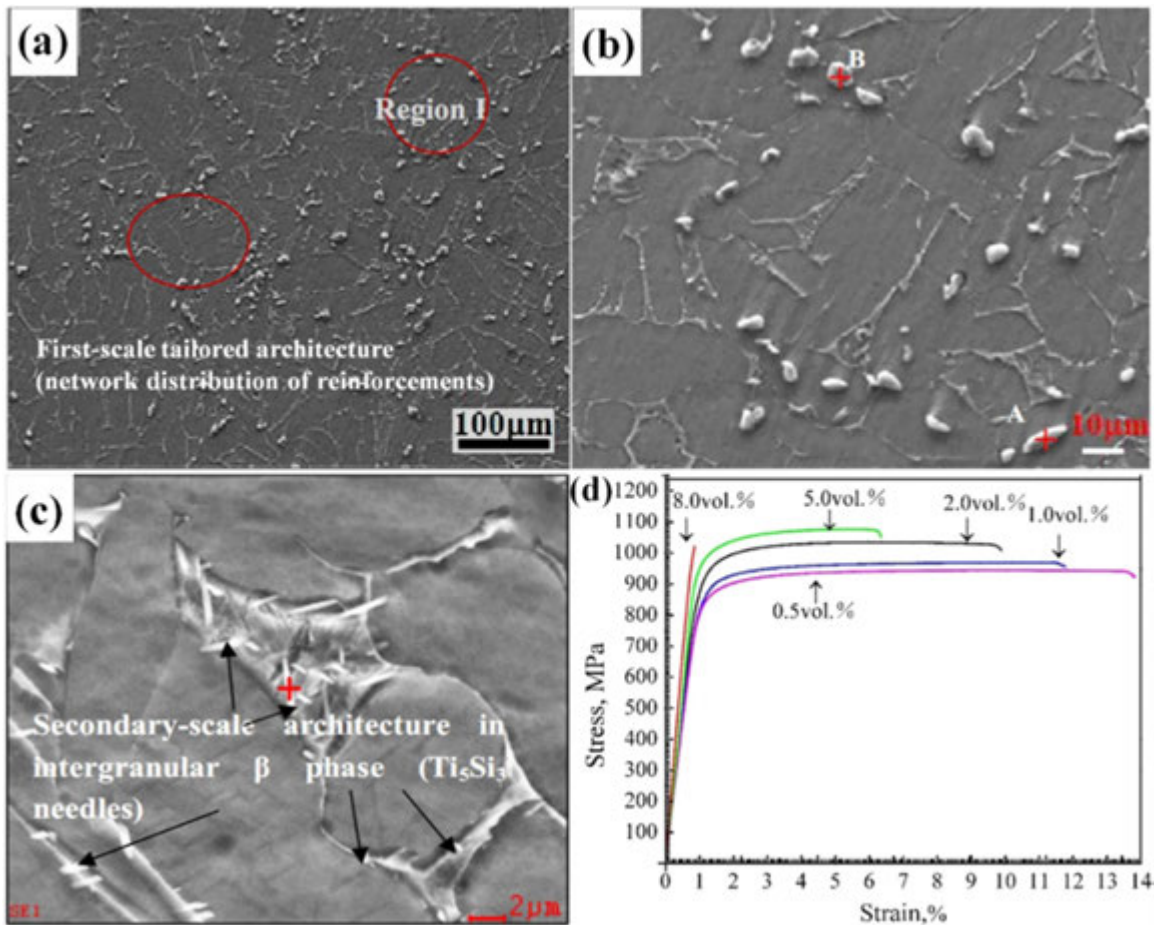


Fig. 13 (a) SEM micrograph (low magnification) of the composite, (b) SEM micrograph of the magnified region I, (c) secondary-scale architecture in intergranular β phase (Ti_5Si_3 needles), and (d) the tensile stress-strain curves of 0.5, 1.0, 2.0, 5.0, 8.0 vol%, $(\text{TiC} + \text{Ti}_3\text{SiC}_2 + \text{Ti}_5\text{Si}_3)/\text{Ti}_6\text{Al}_4\text{V}$ composites. Reproduced from (d) Liu, C., Huang, L.J., Geng, L., Jiao, Y., Tang, A., 2015. In situ synthesis of $(\text{TiC} + \text{Ti}_3\text{SiC}_2 + \text{Ti}_5\text{Si}_3)/\text{Ti}_6\text{Al}_4\text{V}$ composites with tailored two-scale architecture. *Advanced Engineering Materials* 17 (7), 933–941.

and tensile properties of these composites are shown in Fig. 13. The first-scale tailored architecture is the network formed by in-situ Ti_3SiC_2 bars and near equiaxed TiC particles (Fig. 13(a) and (b)), and the secondary-scale architecture is the ultrafine Ti_5Si_3 needles precipitated in intergranular β phase, which was distributed in center matrix particles (Fig. 13(c)). Due to the unique two-scale architecture, the strength of the hybrid $\text{Ti}_6\text{Al}_4\text{V}$ composites were effectively enhanced while maintaining good ductility (8.5%) when the volume fraction of the hybrid reinforcements reached 5 vol% (Fig. 13(d)).

In-situ synthesis of carbonaceous nanomaterials such as CNTs and GNPs in MMCs is an innovative and effective strategy to fabricate advanced MMCs with high performance. This method ensures homogenous dispersion and perfect structural integrity of the carbon nanomaterials after the fabrication process (Tjong, 2013). Powder metallurgy route is usually employed to fabricate these MMCs with in-situ carbon-based nano-reinforcements. According to the different types of the carriers for the in-situ carbonaceous materials, this technique can be categorized into two groups: (1) the direct synthesis of carbon nanomaterials on metal matrix powders (Yang *et al.*, 2011) and (2) synthesis of carbon nanomaterials on the ceramic carriers, such as SiC and Al_2O_3 particles, and then their transfer into the matrix (Li *et al.*, 2014). The former also has two different methods. For transition metal matrix, such as Cu, Fe, Co and Ni, the in-situ carbonaceous nanomaterials can be directly synthesized on these metal powders without using additional catalyst (Tjong, 2013). However, for other metallic matrices without catalytic function, such as Al (He *et al.*, 2007) and Mg (Sun *et al.*, 2013), the additional catalyst should be used to assist the growth of the carbon nanomaterials on the surface of metal powders. The schematic illustration of such a typical fabrication process is shown in Fig. 14(a). This route always involves several steps, first, the additional catalyst particles are decorated on the metal powders through impregnation in the transition metal salt solution followed by drying and calcination in the protective atmosphere. The second step involves in-situ synthesis of the carbon nanomaterials, like CNTs, on metal powders by CVD. Finally, the composites powders containing in-situ carbon materials are compacted, sintered and hot extruded. Sometimes, ball milling is also employed to further disperse these in-situ nano-reinforcements and to promote a better interfacial bonding between metal powders (Yang *et al.*, 2013).

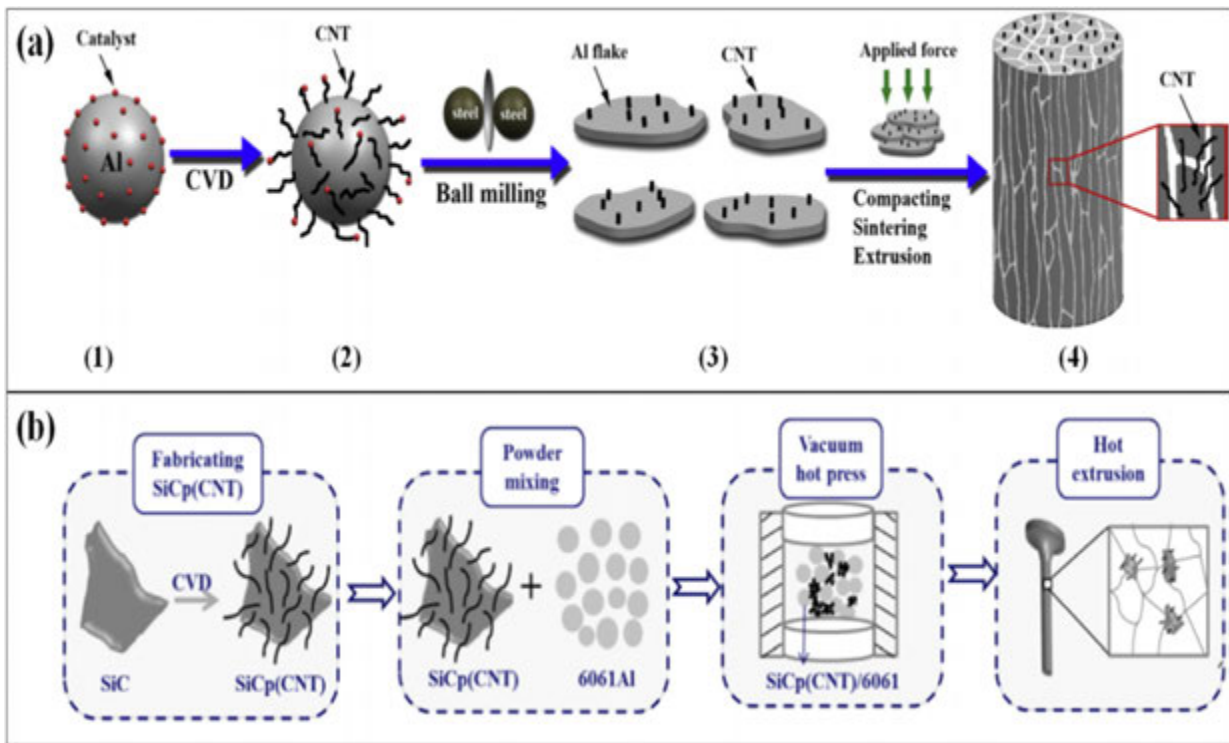


Fig. 14 Schematic illustration of the fabrication procedure of in-situ carbon nanomaterials reinforced MMCs: (a) metal powder carrier, (b) ceramic particle carrier. Reproduced from (a) Yang, X.D., Liu, E.Z., Shi, C.S., *et al.*, 2013. Fabrication of carbon nanotube reinforced Al composites with well-balanced strength and ductility. *Journal of Alloys and Compounds* 563, 216–220. (b) Li, S.S., Su, Y.S., Ouyang, Q., Zhang, D., 2016a. In-situ carbon nanotube-covered silicon carbide particle reinforced aluminium matrix composites fabricated by powder metallurgy. *Materials Letters* 167, 118–121. Li, S.S., Su, Y.S., Zhu, X.H., *et al.*, 2016b. Enhanced mechanical behaviour and fabrication of silicon carbide particles covered by in-situ carbon nanotube reinforced 6061 aluminium matrix composites. *Materials & Design* 107, 130–138.

Utilizing micron ceramic particles as the carrier of in-situ carbon nanomaterials is a promising way to fabricate advanced multi-scale hybrid reinforcements containing MMCs with excellent properties. The schematic is shown in [Fig. 14\(b\)](#), and the process is similar to that of metal powder carrier. The main difference is that the catalyst particles are attached on the surface of the ceramic particle reinforcements rather than on metal matrix powders. Hybrid in-situ CNTs and SiC particles reinforced Al matrix composites ([Li *et al.*, 2016a,b](#)) and hybrid in-situ CNTs and Al_2O_3 particles reinforced Mg matrix composites ([Li *et al.*, 2014](#)) have been successfully prepared by this method, and high mechanical performance of both these types of MMCs were reported.

A novel in-situ method was also proposed to fabricate well-dispersed 3D graphene (GN)/carbon nanotubes hybrid copper nanocomposites ([Zhang *et al.*, 2017a,b,c](#)). [Fig. 15](#) shows the schematic diagram of this innovative method. This method involves in-situ synthesis of 3D graphene network and molecular level mixing. First, the CNTs functionalized with $-\text{COOH}$ were dispersed in the solution of $\text{C}_6\text{H}_6\text{O}_6\text{-Cu}(\text{NO}_3)_2\text{-NaCl}$ under ultrasonication followed by rapid freezing using liquid nitrogen to avoid agglomeration of CNTs. Then, the assembled powders of CNTs- $\text{C}_6\text{H}_6\text{O}_6\text{-Cu}(\text{NO}_3)_2\text{-NaCl}$ were obtained by using the freeze-drying technology. Next, the assembled powders were calcinated and cooled rapidly to room temperature under H_2 atmosphere. The calcinated powder were subsequently washed with deionized water to obtain 3D CNT-GN@Cu powders. The 3D CNT-GN@Cu powders were further coated with copper through an impregnation-calcination-reduction process to achieve a uniform dispersion of 3D CNT-GN in Cu powders. Finally, the 3D CNT-GN/Cu bulk composite was produced by SPS method. A superior combination of strength and ductility was successfully achieved due to the well-dispersed 3D network structure of hybrid CNTs and GN by using this in-situ and molecular level mixing strategy.

Thermo-Mechanical Processing (TMP)

TMP is the set of heating and shaping operations capable of converting traditional materials into high-quality components with enhanced properties ([Verlinden *et al.*, 2007](#)). In general, there are always two direct consequences during TMP: the first one is the desired shape change at macroscopic level, and the other one is the microstructural change on a micro scale. In most cases, TMP can refine grains and eliminate defects, such as shrinkage and pores formed during fabrication process, of metallic materials, resulting in a significantly enhanced mechanical performance. It should be noted that the improvement of microstructure is heavily dependent on processing parameters including temperature, strain, strain rate, deformation mode, lubricants, etc.

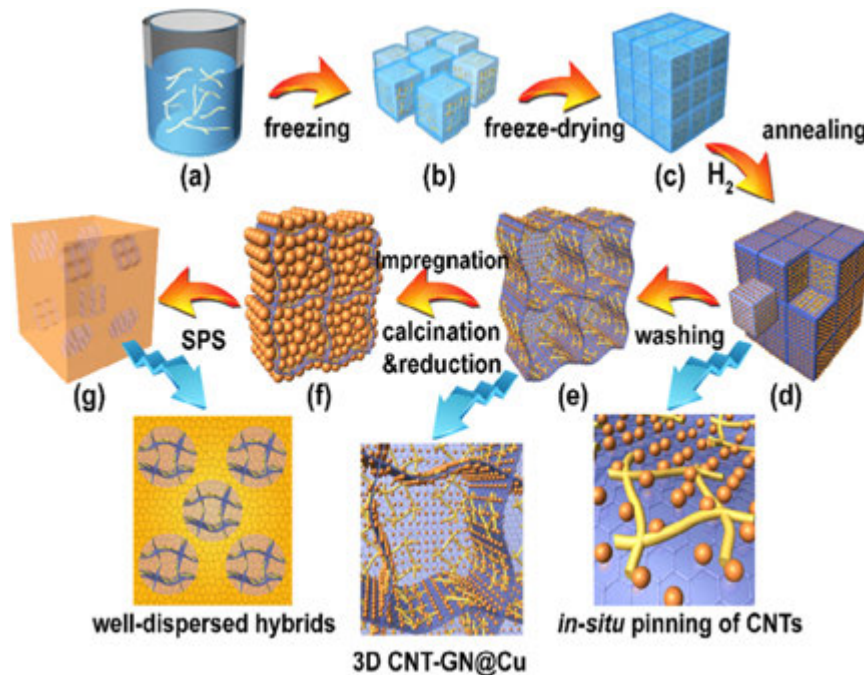


Fig. 15 Schematic illustration of the fabrication process of 3D CNT-GN/Cu bulk materials. (a) Mixed water suspension, (b) rapidly cooled solids and (c) freeze-dried assembled powders of CNTs-C₆H₁₂O₆-Cu(NO₃)₂-NaCl; (d) 3D CNT-GN@Cu NPs coated NaCl powders; (e) 3D CNT-GN@Cu NPs powders; (f) 3D CNT-GN@Cu encapsulated by impregnated reduced Cu particles; (g) 3D CNT-GN/Cu bulk composites. Reproduced from Zhang, L., Wang, Q.D., Liao, W.J., *et al.*, 2017a. Effects of cyclic extrusion and compression on the microstructure and mechanical properties of AZ91D magnesium composites reinforced by SiC nanoparticles. *Materials Characterization* 126, 17–27. Zhang, L., Wang, Q.D., Liao, W.J., *et al.*, 2017b. Microstructure and mechanical properties of the carbon nanotubes reinforced AZ91D magnesium matrix composites processed by cyclic extrusion and compression. *Materials Science and Engineering A* 689, 427–434. Zhang, X., Shi, C.S., Liu, E.Z., *et al.*, 2017c. In-situ space-confined synthesis of well-dispersed three-dimensional graphene/carbon nanotube hybrid reinforced copper nanocomposites with balanced strength and ductility. *Composites Part A: Applied Science and Manufacturing* 103, 178–187.

TMP is an important secondary processing method to improve mechanical properties of MMCs irrespective of whether they are fabricated by solid phase or liquid phase methods. In particular, for MMCs prepared by liquid phase technique, their strength and ductility can be both improved after TMP. According to the degree of the accumulative deformation and grain refinement, we can divide the TMP conducted on MMCs into two types: (1) conventional plastic deformation, and (2) severe plastic deformation.

Conventional Plastic Deformation

As for conventional plastic deformation, there are three commonly used methods, namely, extrusion, rolling and forging. These processing methods are usually conducted at elevated temperatures due to the limited ductility of most of the MMCs.

Extrusion

Extrusion is the most commonly used secondary processing method for MMCs, in which a billet of the MMCs is first placed into an extrusion chamber with a die at one end and a ram on the other. Through the application of force, the billet undergoes a gradual reduction in area through the relatively narrow die to obtain long profiles of constant section determined by the die geometry. **Fig. 16** shows three types of extrusion, namely, direct, conventional, and hydrostatic. In direct extrusion, there is a dead zone near the die where the extruded materials cannot flow. In conventional extrusion, the die is modified to minimize the dead zone, however, the tapered die generates die friction more easily than that of flat die, leading to higher deformation stress at the MMCs/die interface, which may result in material discontinuities like ragged edges. To solve the problem of dead zone and material discontinuities, hydrostatic extrusion is proposed by conducting the extrusion inside a high-pressure fluid. A nearly hydrostatic state and minimal effect of friction in the billet can be achieved in this high-pressure fluid due to the minimized contact area between materials and die.

There are three important factors that need to be critically controlled during extrusion. These include: (1) extrusion ratio, (2) extrusion temperature, and (3) extrusion speed. These factors can significantly affect the mechanical performance of the final extruded MMCs. Wang *et al.* (2011) and Tun and Gupta (2008) found that the distribution of reinforcements whether micron SiC particles or nano Y₂O₃ particles in Mg matrix composites can be improved as the extrusion ratio is increased. In addition, for nano Y₂O₃/Mg composites fabricated by PM, the increased extrusion ratio also reduced the porosity as well as refined grains, leading to enhanced mechanical properties. Extrusion temperature has strong effect on dynamic recrystallization (DRX) of the

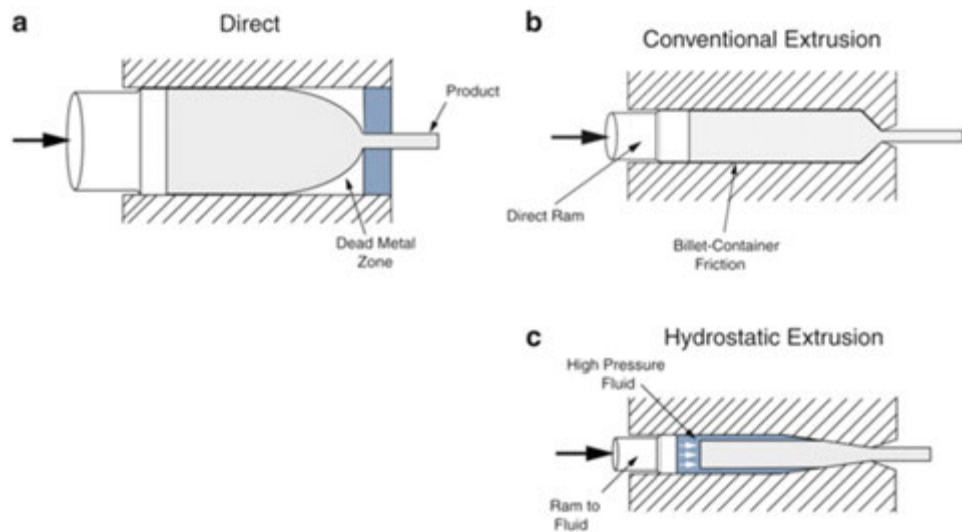


Fig. 16 Three types of extrusion processing: (a) direct, (b) conventional, and (c) hydrostatic. Reproduced from Chawla, N., Chawla, K.K., 2013. *Metal Matrix Composites*, second ed. New York: Springer.

metallic matrix during extrusion. If the extrusion temperature is too low, DRX procedure will not be completed, resulting in many large grains after extrusion; however, high extrusion temperature would induce significant growth of grain size, which has been demonstrated in micron SiC reinforced AZ91 alloy composites (Wang *et al.*, 2011). Extrusion speed can also influence the final mechanical properties of MMCs. Sun *et al.* (2018) investigated the effects of extrusion speed on the mechanical properties and microstructure of the SiCp/AZ91 composite. They revealed that decreasing the extrusion speed (from 1.0 mm/s to 0.01 mm/s) could significantly enhance both yield strength (YS) and ultimate tensile strength (UTS) mainly due to the refinement of the grains and $\text{Mg}_{17}\text{Al}_{12}$ phases precipitates. However, the ductility dropped dramatically which also limited the application of this material. In addition, some researchers have focused on the optimization of extrusion die parameters. For example, Huang *et al.* (2016) investigated the effects of extrusion dies angle on the microstructure and properties of $(\text{TiB} + \text{TiC})/\text{Ti}_6\text{Al}_4\text{V}$ in situ Ti matrix composites. They stated that both tensile strength and ductility were reduced as the extrusion dies angle increased from 45° to 75° , and suggested that the optimal extrusion dies angle should be less than 60° .

Rolling

Rolling is the most important metal working and shaping technique from an economic point of view due to its high productivity. It is used to produce flat and sheet shape components of almost all kinds of common metallic materials, such as steel and aluminum, for a long period. This technique basically involves pushing a metal work-piece into the gap between two rotating rolls, and then the two rolls will simultaneously draw the workpiece and compress it to decrease the thickness and increase the length (as-shown in Fig. 17). Rolling temperature, rolling passes, single pass reduction, and rolling speed are four important factors which can determine the enhancement of mechanical properties during rolling process.

For MMCs, rolling is also one of the important and common TMP methods. Most MMCs are treated by hot rolling due to their limited ductility, but for some MMCs with good ductility, cold rolling is also feasible. This technique is employed to process Al (Kumar *et al.*, 2018), Mg (Liu *et al.*, 2017), Ti (Huang *et al.*, 2012), and Cu (Wang *et al.*, 2020) matrix composites, in which the mechanical properties of these MMCs were all enhanced. Wang *et al.* (2018) systematically investigated the effects of rolling passes and temperatures on the microstructure and mechanical properties of SiCnp/AZ31 nanocomposite. Their results revealed that the matrix grains were refined by progressive DRX, which was enhanced continuously with the increase of rolling passes (reduction). They also found that the nano particles could delay and inhibit the formation of shear bands when compared to AZ31 alloy. The percentage of DRX was improved and the formation of shear bands could be further inhibited as the rolling temperature increased. For mechanical performance, with the increase of the rolling passes, the yield strength enhanced slightly, while the elongation increased first and then decreased. For the sheets with the same rolling reduction, the yield strength reduced and the elongation improved as the rolling temperature increased.

Forging

Forging is the oldest of the metal forming process which can be traced back to 5000–8000 BCE and is also a common TMP method for MMCs including Al (Jin *et al.*, 2020), Mg (Deng *et al.*, 2011) and Ti (Yang *et al.*, 2020) matrix composites. The forging techniques can be roughly categorized into two types: (1) free forging and (2) die forging. The latter one includes several types: (1) open-die forging, (2) closed-die forging, (3) rotary swaging, and (4) rotary forging (Verlinden *et al.*, 2007).

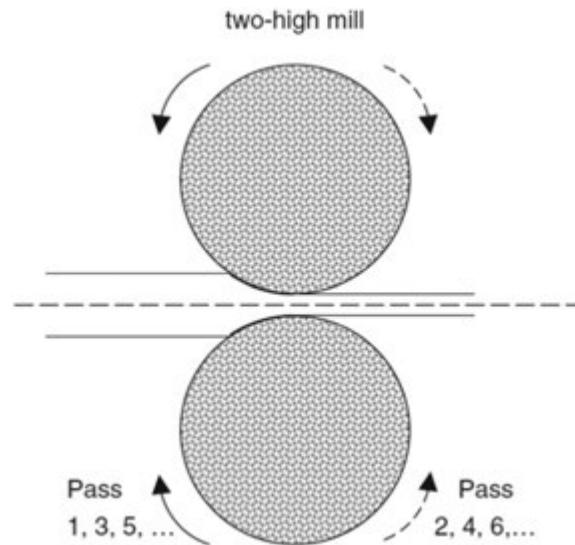


Fig. 17 Schematic of a 2-high mill rolling. Reproduced from Verlinden, B., Driver, J., Samajdar, I., Doherty, R.D., 2007. Thermo-Mechanical Processing of Metallic Materials, first ed. Oxford: Pergamon.

Severe Plastic Deformation

The conventional TMP methods mentioned above cannot be used to produce materials with ultrafine grains (UFG, average grain size less than $\sim 1 \mu\text{m}$) due to the limitation on the overall strains. Accordingly, attention has been focused on the development of novel techniques which can prepare ultrafine-grained materials with grain sizes in the sub-micrometer and the nanometer range. To achieve this goal, there are two different approaches, namely, (1) “bottom-up” route and (2) “top down” route. In the bottom-up approach, UFG materials are obtained by assembling individual atoms or by consolidating nanoparticle solids. The top-down approach relies on imposing large amount of strain or shock loading, which can avoid the small product sizes and the contamination when compared to the bottom-up approach.

Formally, the main feature of severe plastic deformation (SPD) is that very high strain is imposed on a bulk material without any significant change in the overall dimensions of the material resulting in excellent grain refinement. To date, many different SPD processing techniques have been developed, and for MMCs, equal channel angular pressing (ECAP), high-pressure torsion (HPT), accumulative roll bonding (ARB), friction stir processing (FSP), cyclic extrusion and compressing (CEC), and multi-directional forging (MDF) have been extensively reported.

Equal channel angular pressing

The ECAP was first introduced in the 1970s and 1980s to develop a metal forming process where high strains can be imposed into metal billets by simple shear. However, the potential of this method for preparing UFG materials was not exploited until 1990s (Valiev and Langdon, 2006). Similar to conventional TMP methods, the mechanical properties of ECAPed materials are also strongly affected by pressing passes, pressing temperature, pressing speed, and the die parameters including the channel angle (Φ) and the angle of curvature (Ψ) (as shown in Fig. 18(a)). The main difference is that the processing routes in ECAP also have significant effects on the microstructure evolution and mechanical properties of the final billets. There are four basic processing routes which are illustrated in Fig. 18(b). From extensive studies, the results revealed that route Bc might be the superior one to realize homogenous microstructure.

More and more attentions have been paid to utilize ECAP for processing MMCs. The effects of ECAP on microstructure evolution and mechanical properties of Al (Ramu and Bauri, 2009), Mg (Qiao *et al.*, 2016), Ti (Han *et al.*, 2015), and Cu (Wang *et al.*, 2013) matrix composites have been investigated. Similar conclusions could be drawn that intense plastic strain introduced by ECAP has a potential for both refining the grain size of metal matrix (even to submicrometer or nano meter level) and in significantly improving the strength of the composites. In some cases, the strength and ductility were enhanced simultaneously by choosing suitable processing parameters. In addition, there are also some interesting phenomena: (1) ECAP can effectively improve the homogeneity of the distribution of nano-reinforcements due to large shear force thus leading to an enhancement in mechanical properties of an MMC with clusters of reinforcements (Sabirov *et al.*, 2005) and (2) although large shear force was introduced during ECAP, there was little or no breaking of the particulates, like Al_2O_3 , after processing. The minimized cracking possibility of particulates might be attributed to no confining aperture and thus no reduction in the sample cross-section as it passes through the die (Valiev *et al.*, 1998).

High-pressure torsion

HPT is another important “top-down” SPD technique which has similar mechanical performance enhancing effects as that of ECAP. Its schematic diagram is as shown in Fig. 19. The disk sample is located between two anvils where it is subjected to a

compressive applied pressure, P , of several GPa at room temperature or at an elevated temperature and simultaneously it is subjected to a torsional strain which is imposed through rotation of the lower anvil. Surface frictional forces therefore deform the disk by shear so that deformation proceeds under a quasi-hydrostatic pressure (Zhilyaev and Langdon, 2008). In this technique, the final properties of the processed materials are strongly dependent on the applied load and the number of rotations (the imposed strain).

This technique has also been utilized to refine matrix grains and to optimize the distribution of reinforcements for Al (Valiev *et al.*, 1998), Mg (Chen *et al.*, 2015), Ti (Li *et al.*, 2018), and Cu (Islamgaliev *et al.*, 2001) matrix composites. In particular, Chen *et al.* (2015) applied HPT to improve the mechanical performance of Mg-2Zn composite containing 14 vol% nano SiC particles.

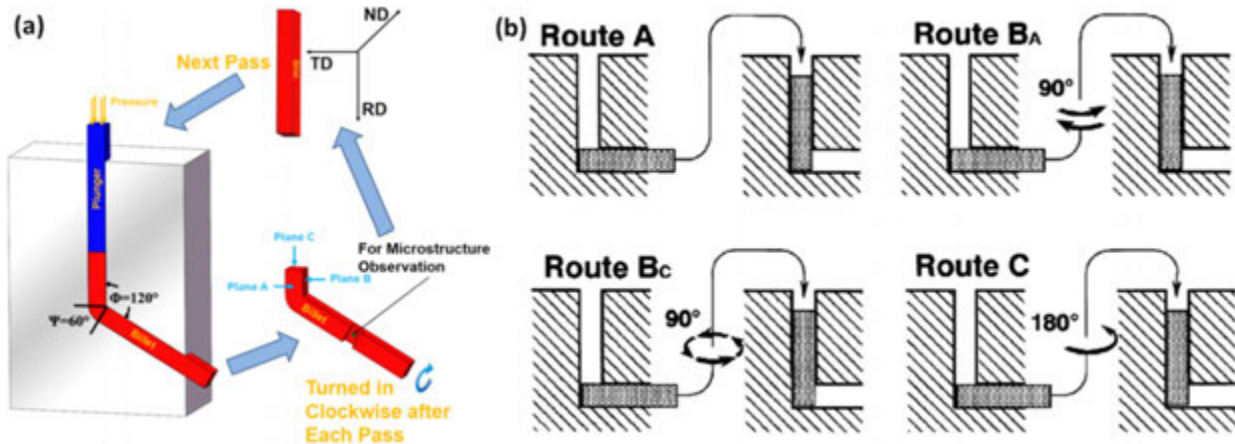


Fig. 18 (a) Schematic diagram of the ECAP process, and (b) The four fundamental processing routes in ECAP. Reproduced from (a) Xiang, J., Han, Y.F., Huang, G.F., *et al.*, 2019a. Microstructural evolution in titanium matrix composites processed by multi-pass equal-channel angular pressing. *Journal of Materials Science* 54 (10), 7931–7942. Xiang, Y.Y., Wang, X.J., Hu, X.S., *et al.*, 2019b. Achieving ultra-high strengthening and toughening efficiency in carbon nanotubes/magnesium composites via constructing micro-nano layered structure. *Composites Part A: Applied Science and Manufacturing* 119, 225–234. (b) Valiev, R.Z., Langdon, T.G., 2006. Principles of equal-channel angular pressing as a processing tool for grain refinement. *Progress in Materials Science* 51 (7), 881–981.

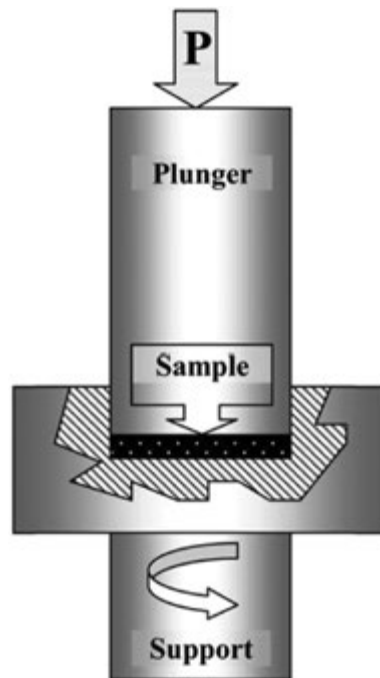


Fig. 19 Schematic diagram of HPT processing. Reproduced from Zhilyaev, A., Langdon, T., 2008. Using high-pressure torsion for metal processing: Fundamentals and applications. *Progress in Materials Science* 53 (6), 893–979.

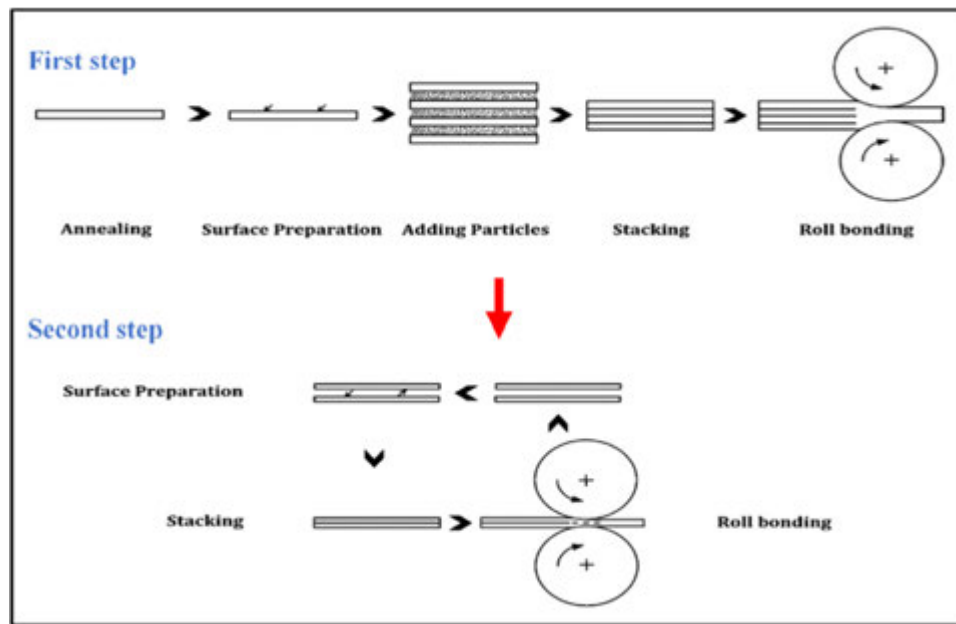


Fig. 20 Schematic procedure to produce MMCs via ARB process. Reproduced from Baazamat, S., Tajally, M., Borhani, E., 2015. Fabrication and characteristic of Al-based hybrid nanocomposite reinforced with WO_3 and SiC by accumulative roll bonding process. *Journal of Alloys Compounds* 653, 39–46.

After HPT processing, this material achieved remarkable yield strength of 710 ± 35 MPa (the highest yield strength reported for Mg based materials). In addition, the plastic strain of over 40% was also obtained, indicating an excellent combination of ultrahigh strength and ductility of this HPTed composite. Therefore, this method has great potential to be used for improving energy efficiency and system performance in numerous applications.

Accumulative roll bonding

ARB processing is another novel SPD method, also known as sandwich processing, which can be used to produce MMCs with ultra-fine grains (Ghalehbandi *et al.*, 2019). Fig. 20 shows steps involved in ARB and include: (1) annealing the metal strips or sheets, (2) surface preparation through degreasing by acetone and scratching with a steel brush, (3) adding reinforcements, (4) stacking, and (5) roll bonding. In the third step, the reinforcements, especially nano-reinforcements, are usually dispersed in the dispersion solution, and subsequently sprayed onto the surfaces of the metal strips or sheets followed by drying in the air (Yoo *et al.*, 2012). Electrophoretic deposition can also be used to disperse the reinforcements onto the metal strips, which has been demonstrated in the study on CNTs reinforced Mg (Xiang *et al.*, 2019a,b) and Cu (Meng *et al.*, 2018) matrix composites prepared by electrophoretic deposition and hot rolling. Baazamat *et al.* (2015) produced hybrid WO_3 and SiC nanoparticles reinforced Al matrix nanocomposites through ARB process, and the results revealed that after 9 cycles, the hybrid nanocomposites exhibited an excellent distribution of the nanoparticles with good interfacial bonding between the reinforcements and the matrix. This technique may become popular for fabricating advanced MMCs with high performance due to its ease of processing (Bakshi *et al.*, 2010).

A unique technology combining anodizing and accumulative rolling bonding is used to fabricate in-situ Al_2O_3 reinforced Al matrix composites. This method always involves the following steps: (1) the Al strips are anodized to form in-situ Al_2O_3 on the surfaces of the strips after annealing treatment followed by degreasing, (2) dispersion of the ex-situ reinforcements on the surfaces of the anodized Al strips uniformly, (3) the surface preparation for non-anodized Al strips, (4) stacking of the anodized Al strips with ex-situ reinforcements and non-anodized Al strips and (5) accumulative rolling bonding. Hybrid $\text{Al}_2\text{O}_{3\text{in-situ}} + \text{ZrC}_{\text{ex-situ}}$ (Shamanian *et al.*, 2015), $\text{Al}_2\text{O}_{3\text{in-situ}} + \text{CNTs}_{\text{ex-situ}}$ (Nasresfahani and Shamanian, 2018), $\text{Al}_2\text{O}_{3\text{in-situ}} + \text{TiC}_{\text{ex-situ}}$ (Farajzadeh Dehkordi *et al.*, 2013), and $\text{Al}_2\text{O}_{3\text{in-situ}} + \text{SiC}_{\text{ex-situ}}$ (Ahmadi *et al.*, 2013) reinforced Al matrix composites were successfully fabricated using this method.

Friction stir processing

Friction stir processing, derived from the modification of friction stir welding, is a novel severe plastic deformation (SPD) technique. The main idea of this method is to disperse reinforcements uniformly in metallic matrix and refine grain size via the rotation of tool pin. To produce MMCs, there are two ways to place the reinforcements. A long groove is cut on the surface of the metallic matrix in the path of tool followed by filling with reinforcements and treating with FSP as shown in Fig. 21(a). Alternatively, reinforcements are introduced into the cavities drilled in a metallic plate followed by FSP as shown in Fig. 21(b). Eskandari *et al.* (2016) successfully fabricated hybrid TiB_2 particles and Al_2O_3 particles reinforced Al matrix composites using FSP and found that the wear resistance of

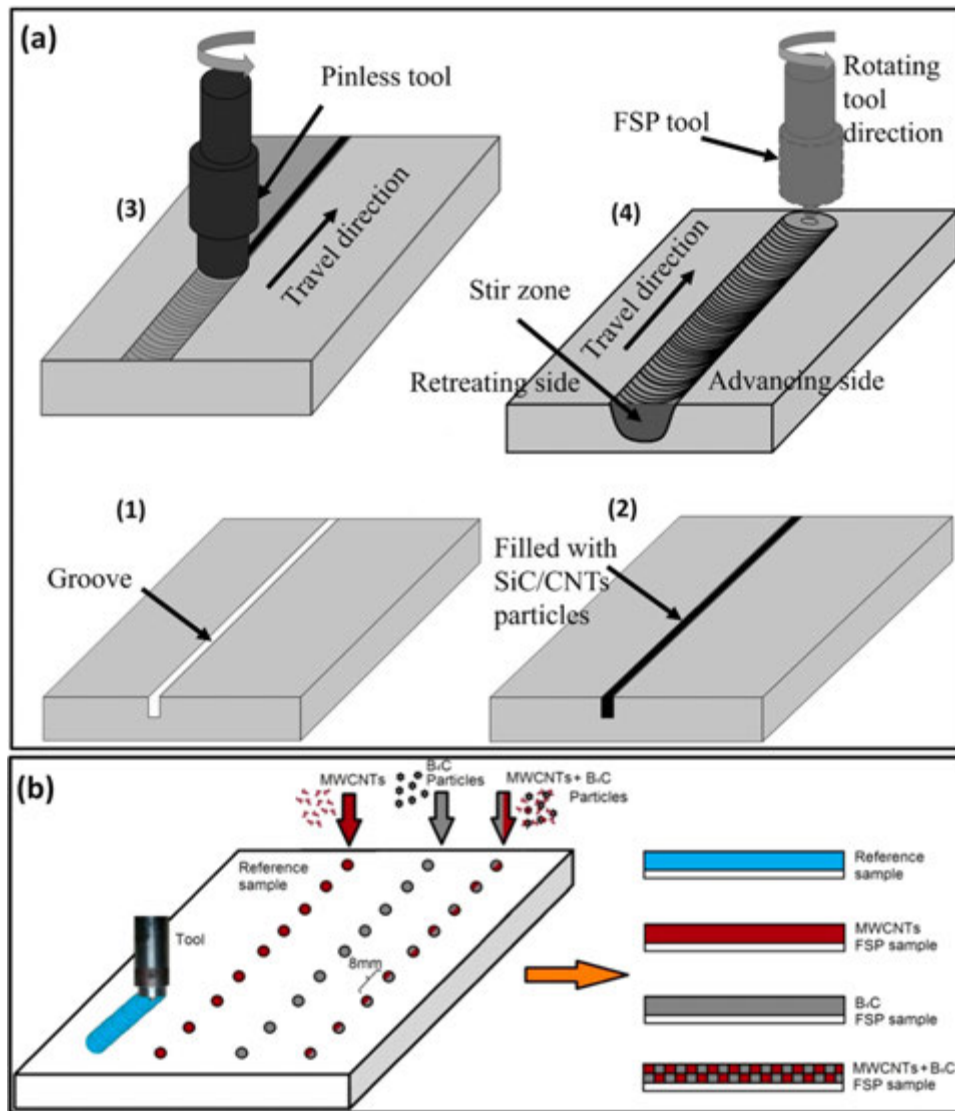


Fig. 21 Schematic diagram of FSP using different reinforcements incorporating methods: (a) grooves and (b) cavities. Reproduced from (a) Jain, V.K.S., Yazar, K.U., Muthukumar, S., 2019. Development and characterization of Al5083-CNTs/SiC composites via friction stir processing. *Journal of Alloys and Compounds* 798 (25), 82–92. (b) Khan, M., Rehman, A., Aziz, T., *et al.*, 2017. Cold formability of friction stir processed aluminium composites containing carbon nanotubes and boron carbide particles. *Materials Science and Engineering A* 701 (31), 382–388.

the processed hybrid nanocomposites over the un-reinforced matrix alloy was improved by more than eight times due to the homogeneous distribution of the hybrid reinforcements. A similar result was also reported in a study on hybrid ZrSiO_4 and Al_2O_3 reinforced Mg matrix composites prepared by using FSP (Sharifitabar *et al.*, 2016). Moreover, FSP is also an effective technique for secondary mechanical treatment for the MMCs in order to obtain uniform distribution of reinforcements, especially nano-reinforcements, like CNTs (Liu *et al.*, 2014) or GNPs (Ajay Kumar *et al.*, 2020), in the metallic matrix.

Cyclic extrusion and compression

Fig. 22 shows the schematic diagram of CEC technique. The characteristics of this method are as follows: (1) extrusion and compression can be carried out simultaneously, which is helpful to eliminate the defects in the billets; (2) the compressive stress state can prevent the crack initiation and growth; (3) it can be processed continuously without changing the original shape of the billets; (4) the large strain imposed by CEC can lead to a remarkable refinement of grains. This technique has a wide range of applications, and it can be directly used to process ingots or powders to obtain bulk materials with fine grains and excellent mechanical properties. This method is also used to improve the mechanical performance of CNTs/Mg (Zhang *et al.*, 2017a,b,c) and SiC/Mg (Guo *et al.*, 2012) composites.

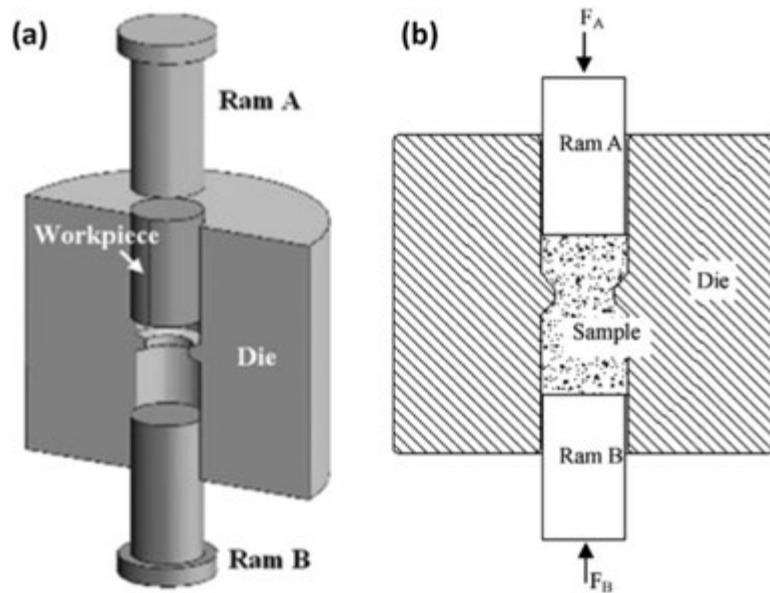


Fig. 22 Schematic illustrations of (a) CEC apparatus and (b) the cross-section of (a). Reproduced from (a) Zhang, L., Wang, Q.D., Liao, W.J., *et al.*, 2017a. Effects of cyclic extrusion and compression on the microstructure and mechanical properties of AZ91D magnesium composites reinforced by SiC nanoparticles. *Materials Characterization* 126, 17–27. Zhang, L., Wang, Q.D., Liao, W.J., *et al.*, 2017b Microstructure and mechanical properties of the carbon nanotubes reinforced AZ91D magnesium matrix composites processed by cyclic extrusion and compression. *Materials Science and Engineering A* 689, 427–434. Zhang, X., Shi, C.S., Liu, E.Z., *et al.*, 2017c. In-situ space-confined synthesis of well-dispersed three-dimensional graphene/carbon nanotube hybrid reinforced copper nanocomposites with balanced strength and ductility. *Composites Part A: Applied Science and Manufacturing* 103, 178–187. (b) Wang, Q.D., Chen, Y.J., Liu, M.P., Lin, J.B., Roven, H.J., 2010. Microstructure evolution of AZ series magnesium alloys during cyclic extrusion compression. *Materials Science and Engineering A* 527 (9), 2265–2273.

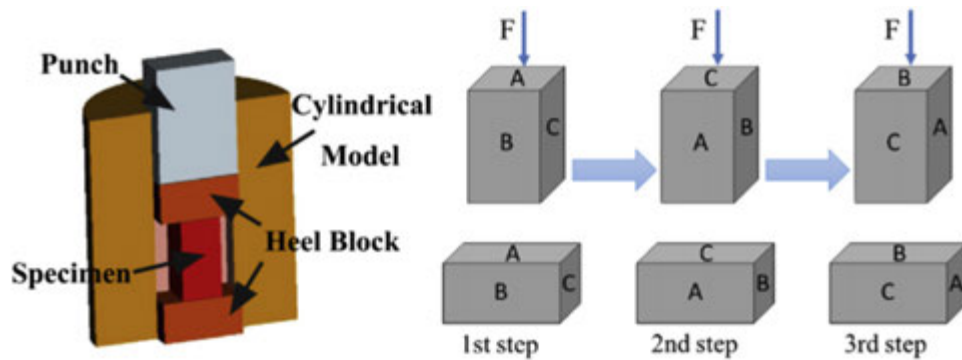


Fig. 23 Schematic illustrations of multi-directional forging. Reproduced from Lü, Z.D., Zhang, C.J., Feng, H., *et al.*, 2019. Effect of heat treatment on microstructure and tensile properties of 2 vol% TiCp/near- β Ti composite processed by isothermal multidirectional forging. *Materials Science and Engineering A* 761, 138064.

Multi-directional forging

MDF is a simple SPD technique. The schematic illustrations of MDF is shown in Fig. 23. From the figure, it can be seen that the direction of applied load changes along the three axial directions of the billets during MDF processing. The billet is deformed repeatedly according to the direction of the applied load, but its dimension nearly stays unchanged. Thus, the essence of MDF is multi-pass free forging in different directions along the billets. This method is successfully used for the optimization of mechanical properties for Mg (Nie *et al.*, 2015) and Ti (Lü *et al.*, 2019) matrix composites.

Summary and Outlook

This article illustrates that solid phase processing techniques can fabricate MMCs with fine (even ultrafine) grains, homogeneous distribution of reinforcements and appropriate interfacial bonding, thus, resulting in high mechanical performance. It is

undeniable that this field has been instrumental in realizing significant achievements in recent times. However, there are still some big challenges which can hinder the wide applications of these technologies in the field of MMCs. Compared with liquid phase approach, the solid phase approaches involve more complicated steps and lower mass production capability leading to much higher cost of production. In addition, for nano metal matrix composites (NMMCs), the content of the nano-reinforcements, such as nano ceramic particles, CNTs and GNPs, still remained at a relatively low level (usually less than 5 vol%) due to the action of strong van der Waals' forces, which strongly limits the significant enhancement in mechanical properties of NMMCs. Therefore, researchers may need to pay more attention to the following two aspects: (1) simplify the preparation process of solid phase techniques to effectively improve the economics of the process. For example, some simulation methods or machine learning or artificial intelligence can be employed for preliminary exploration to decrease the number of attempts and reduce experimental costs and (2) in order to achieve high volume fraction of uniformly dispersed nano-reinforcements in metallic matrix, some novel and efficient dispersing methods can be further explored.

References

- Agarwal, A., Bakshi, S.R., Lahiri, D., 2011. Carbon Nanotube Reinforced Metal Matrix Composites, first ed. Boca Raton: CRC Press.
- Ahmadi, A., Toroghinejad, M.R., Najafizadeh, A., 2013. Evaluation of microstructure and mechanical properties of Al/Al₂O₃/SiC hybrid composite fabricated by accumulative roll bonding process. *Materials & Design* 53 (1), 13–19.
- Ajay Kumar, P., Madhu, H.C., Abhishek, P., *et al.*, 2020. Friction stir processing of squeeze cast A356 with surface compacted graphene nanoplatelets (GNPs) for the synthesis of metal matrix composites. *Materials Science and Engineering A* 769, 138517.
- Andrews, R., Jacques, D., Minot, M., Rantell, T., 2002. Fabrication of carbon multiwall nanotube/polymer composites by shear mixing. *Macromolecular Materials and Engineering* 287, 395–403.
- Azarniya, A., Azarniya, A., Sovizi, S., *et al.*, 2017. Physicomechanical properties of spark plasma sintered carbon nanotube-reinforced metal matrix nanocomposites. *Progress in Materials Science* 90, 276–324.
- Baazamat, S., Tajally, M., Borhani, E., 2015. Fabrication and characteristic of Al-based hybrid nanocomposite reinforced with WO₃ and SiC by accumulative roll bonding process. *Journal of Alloys Compounds* 653, 39–46.
- Bakshi, S.R., Lahiri, D., Agarwal, A., 2010. Carbon nanotube reinforced metal matrix composites – A review. *International Materials Reviews* 55 (1), 41–64.
- Chattopadhyay, P., Manna, I., Talapatra, S., Pabi, S., 2001. A mathematical analysis of milling mechanics in a planetary ball mill. *Materials Chemistry and Physics* 68, 85–94.
- Chawla, N., Chawla, K.K., 2013. Metal Matrix Composites, second ed. New York: Springer.
- Chen, L.Y., Xu, J.Q., Choi, H., *et al.*, 2015. Processing and properties of magnesium containing a dense uniform dispersion of nanoparticles. *Nature* 528 (7583), 539–543.
- Chen, W.X., Lee, J.Y., Liu, Z., 2003. The nanocomposites of carbon nanotube with Sb and SnSb_{0.5} as Li-ion battery anodes. *Carbon* 41 (5), 959–966.
- Cundall, P.A., Strack, O.D., 1979. A discrete numerical model for granular assemblies. *Geotechnique* 29, 47–65.
- Dallimore, M., McCormick, P., 1996. Dynamics of planetary ball milling: A comparison of computer simulated processing parameters with CuO/Ni displacement reaction milling kinetics. *Materials Transactions* 37, 1091–1098.
- Deng, K.K., Wang, X.J., Gan, W.M., *et al.*, 2011. Isothermal forging of AZ91 reinforced with 10 vol% silicon carbon particles. *Materials Science and Engineering A* 528 (3), 1707–1712.
- Eskandari, H., Taheri, R., Khodabakhshi, F., 2016. Friction-stir processing of an AA8026-TiB₂-Al₂O₃ hybrid nanocomposite: Microstructural developments and mechanical properties. *Materials Science and Engineering A* 660 (13), 84–96.
- Farajzadeh Dehkordi, H., Toroghinejad, M.R., Raeissi, K., 2013. Fabrication of Al/Al₂O₃/TiC hybrid composite by anodizing and accumulative roll bonding processes and investigation of its microstructure and mechanical properties. *Materials Science and Engineering A* 585, 460–467.
- Ghalehbandi, S.M., Malaki, M., Gupta, M., 2019. Accumulative roll bonding – A review. *Applied Sciences* 9 (17), 3627–3659.
- Guo, W., Wang, Q.D., Ye, B., *et al.*, 2012. Microstructural refinement and homogenization of Mg–SiC nanocomposites by cyclic extrusion compression. *Materials Science and Engineering A* 556, 267–270.
- Gupta, M., Wong, W.L.E., 2005. Enhancing overall mechanical performance of metallic materials using two-directional microwave assisted rapid sintering. *Scripta Materialia* 52 (6), 479–483.
- Gupta, M., Sharon, N.M.L., 2011. Magnesium, Magnesium Alloys, and Magnesium Composites, first ed. New Jersey: John Wiley & Sons.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.
- Han, Y.F., Li, J.X., Huang, G.F., *et al.*, 2015. Effect of ECAP numbers on microstructure and properties of titanium matrix composite. *Materials & Design* 75, 113–119.
- He, C.N., Zhao, N.Q., Shi, C.S., *et al.*, 2007. An approach to obtaining homogeneously dispersed carbon nanotubes in Al powders for preparing reinforced Al-matrix composites. *Advanced Materials* 19 (8), 1128–1132.
- Huang, G.F., Guo, X.L., Han, Y.F., *et al.*, 2016. Effect of extrusion dies angle on the microstructure and properties of (TiB + TiC)/Ti₆Al₄V in situ titanium matrix composite. *Materials Science and Engineering A* 667, 317–325.
- Huang, L.J., Cui, X.P., Geng, L., Fu, Y., 2012. Effects of rolling deformation on microstructure and mechanical properties of network structured TiBw/Ti composites. *Transactions of Nonferrous Metals Society of China* 22, s79–s83.
- Ibrahim, I.A., Mohamed, F.A., Lavernia, E.J., 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science* 26, 1137–1156.
- Islamgaliev, R.K., Buchgraber, W., Kolobov, Y.R., *et al.*, 2001. Deformation behavior of Cu-based nanocomposite processed by severe plastic deformation. *Materials Science and Engineering A* 319–321, 872–876.
- Jiang, L., Fan, G.L., Li, Z.Q., *et al.*, 2011. An approach to the uniform dispersion of a high volume fraction of carbon nanotubes in aluminum powder. *Carbon* 49 (6), 1965–1971.
- Jiang, L., Li, Z.Q., Fan, G.L., Cao, L.L., Zhang, D., 2012. The use of flake powder metallurgy to produce carbon nanotube (CNT)/aluminum composites with a homogenous CNT distribution. *Carbon* 50 (5), 1993–1998.
- Jiang, Y.Y., Tan, Z.Q., Xu, R., *et al.*, 2018. Tailoring the structure and mechanical properties of graphene nanosheet/aluminum composites by flake powder metallurgy via shift-speed ball milling. *Composites Part A: Applied Science and Manufacturing* 111, 73–82.
- Jin, X.Z., Xu, W.C., Yang, G.J., *et al.*, 2020. Tuning microstructure and mechanical properties of squeeze-cast whisker-reinforced 2024Al composites by hot forging process design. *Materials Characterization* 164, 110322.
- Kumar, R.V., Keshavamurthy, R., Perugu, C.S., *et al.*, 2018. Influence of hot rolling on microstructure and mechanical behaviour of Al6061-ZrB₂ in-situ metal matrix composites. *Materials Science and Engineering A* 738, 344–352.
- Li, F.X., Hao, P.D., Yi, J.H., *et al.*, 2018. Microstructure and strength of nano-/ultrafine-grained carbon nanotube-reinforced titanium composites processed by high-pressure torsion. *Materials Science and Engineering A* 722, 122–128.

- Li, H.P., Fan, J.W., Geng, X.X., *et al.*, 2014. Alumina powder assisted carbon nanotubes reinforced Mg matrix composites. *Materials & Design* 60, 637–642.
- Li, S.S., Su, Y.S., Ouyang, Q., Zhang, D., 2016a. In-situ carbon nanotube-covered silicon carbide particle reinforced aluminium matrix composites fabricated by powder metallurgy. *Materials Letters* 167, 118–121.
- Li, S.S., Su, Y.S., Zhu, X.H., *et al.*, 2016b. Enhanced mechanical behaviour and fabrication of silicon carbide particles covered by in-situ carbon nanotube reinforced 6061 aluminium matrix composites. *Materials & Design* 107, 130–138.
- Li, Z., Fan, G.L., Guo, Q., *et al.*, 2015. Synergistic strengthening effect of graphene-carbon nanotube hybrid structure in aluminium matrix composites. *Carbon* 95, 419–427.
- Liu, C., Huang, L.J., Geng, L., Jiao, Y., Tang, A., 2015. In situ synthesis of $(\text{TiC} + \text{Ti}_3\text{SiC}_2 + \text{Ti}_5\text{Si}_3)/\text{Ti6Al4V}$ composites with tailored two-scale architecture. *Advanced Engineering Materials* 17 (7), 933–941.
- Liu, W.Q., Wang, X.J., Hu, X.S., Wu, K., Zheng, M.Y., 2017. Effects of hot rolling on microstructure, macrotexture and mechanical properties of pre-extruded AZ31/SiC nanocomposite sheets. *Materials Science and Engineering A* 683, 15–23.
- Liu, Z.Y., Xiao, B.L., Wang, W.G., Ma, Z.Y., 2014. Analysis of carbon nanotube shortening and composite strengthening in carbon nanotube/aluminum composites fabricated by multi-pass friction stir processing. *Carbon* 69, 264–274.
- Lü, Z.D., Zhang, C.J., Feng, H., *et al.*, 2019. Effect of heat treatment on microstructure and tensile properties of 2 vol% TiCp/near- β Ti composite processed by isothermal multidirectional forging. *Materials Science and Engineering A* 761, 138064.
- Ma, Z.Y., Li, J.H., Li, S.X., *et al.*, 1996. Property-microstructure correlation in in situ formed Al_2O_3 , TiB_2 and Al_3Ti mixture-reinforced aluminium composites. *Journal of Materials Science* 31 (3), 741–747.
- Meng, L.L., Wang, X.J., Ning, J.L., *et al.*, 2018. Beyond the dimensional limitation in bio-inspired composite: Insertion of carbon nanotubes induced laminated Cu composite and the simultaneously enhanced strength and toughness. *Carbon* 130, 222–232.
- Miracle, D.B., 2005. Metal matrix composites – From science to technological significance. *Composites Science and Technology* 65, 2526–2540.
- Mortensen, A., Llorca, J., 2010. Metal matrix composites. *Annual Review of Materials Research* 9, 1–16.
- Nasrestahani, M.R., Shamanian, M., 2018. Development and characterization of Al/MWCNT- Al_2O_3 hybrid composite by accumulative roll bonding. *Journal of Materials Science* 53 (15), 10812–10821.
- Nie, K.B., Wang, X.J., Xu, F.J., Zheng, M.Y., 2015. Microstructure and tensile properties of SiC nanoparticles reinforced magnesium matrix composite prepared by multidirectional forging under decreasing temperature conditions. *Materials Science and Engineering A* 639, 465–473.
- Qiao, X.G., Ying, T., Zheng, M.Y., *et al.*, 2016. Microstructure evolution and mechanical properties of nano-SiCp/AZ91 composite processed by extrusion and equal channel angular pressing (ECAP). *Materials Characterization* 121, 222–230.
- Ramu, G., Bauri, R., 2009. Effect of equal channel angular pressing (ECAP) on microstructure and properties of Al-SiCp composites. *Materials & Design* 30 (9), 3554–3559.
- Sabirov, I., Kolednik, O., Valiev, R.Z., *et al.*, 2005. Equal channel angular pressing of metal matrix composites: Effect on particle distribution and fracture toughness. *Acta Materialia* 53 (18), 4919–4930.
- Shamanian, M., Mohammadzadeh, M., Asgari, H., Szpunar, J., 2015. Fabrication and characterization of Al- Al_2O_3 -ZrC composite produced by accumulative roll bonding (ARB) process. *Journal of Alloys Compounds* 618, 19–26.
- Sharifitabar, M., Kasheli, M., Khorshahian, S., 2016. Effect of friction stir processing pass sequence on properties of Mg-ZrSiO₄- Al_2O_3 surface hybrid micro/nano-composites. *Materials & Design* 108 (15), 1–7.
- Sun, F.J., Shi, C.S., Rhee, K.Y., Zhao, N.Q., 2013. In situ synthesis of CNTs in Mg powder at low temperature for fabricating reinforced Mg composites. *Journal of Alloys and Compounds* 551, 496–501.
- Sun, X.F., Wang, C.J., Deng, K.K., *et al.*, 2018. High strength SiCp/AZ91 composite assisted by dynamic precipitated $\text{Mg}_{17}\text{Al}_{12}$ phase. *Journal of Alloys and Compounds* 732, 328–335.
- Suryanarayana, C., 2001. Mechanical alloying and milling. *Progress in Materials Science* 46, 1–184.
- Suryanarayana, C., 2004. *Mechanical Alloying and Milling*, first ed. New York: Marcel Dekker.
- Tjong, S.C., 2013. Recent progress in the development and properties of novel metal matrix nanocomposites reinforced with carbon nanotubes and graphene nanosheets. *Materials Science and Engineering R* 74, 281–350.
- Tjong, S.C., Ma, Z.Y., 2000. Microstructural and mechanical characteristics of in situ metal matrix composites. *Materials Science and Engineering R* 29 (3), 49–113.
- Tun, K.S., Gupta, M., 2008. Effect of extrusion ratio on microstructure and mechanical properties of microwave-sintered magnesium and $\text{Mg/Y}_2\text{O}_3$ nanocomposite. *Journal of Materials Science* 43, 4503–4511.
- Valiev, R.Z., Langdon, T.G., 2006. Principles of equal-channel angular pressing as a processing tool for grain refinement. *Progress in Materials Science* 51 (7), 881–981.
- Valiev, R.Z., Islamgaliev, R.K., Kuzmina, N.F., *et al.*, 1998. Strengthening and grain refinement in an Al-6061 metal matrix composite through intense plastic straining. *Scripta Materialia* 40 (1), 117–122.
- Verlinden, B., Driver, J., Samajdar, I., Doherty, R.D., 2007. *Thermo-Mechanical Processing of Metallic Materials*, first ed. Oxford: Pergamon.
- Wai, W., Eugene, L., Gupta, M., 2010. Characteristics of aluminium and magnesium based nanocomposites processed using hybrid microwave sintering. *Journal of Microwave Power and Electromagnetic Energy* 44 (1), 14–27.
- Wang, G.S., Fan, G.H., Geng, L., Hu, W., Huang, Y.D., 2013. Microstructure evolution and mechanical properties of TiB_2/Cu composites processed by equal channel angular pressing at elevated temperature. *Materials Science and Engineering A* 571, 144–149.
- Wang, M., Sheng, J., Wang, L.D., *et al.*, 2020. Hot rolling behavior of graphene/Cu composites. *Journal of Alloys and Compounds* 816, 153204.
- Wang, X.J., Xu, J., Hu, X.S., *et al.*, 2011. Influences of extrusion parameters on microstructure and mechanical properties of particulate reinforced magnesium matrix composites. *Materials Science and Engineering A* 528, 6387–6392.
- Wang, X.J., Liu, W.Q., Hu, X.S., Wu, K., 2018. Microstructural modification and strength enhancement by SiC nanoparticles in AZ31 magnesium alloy during hot rolling. *Materials Science and Engineering A* 715, 49–61.
- Wei, S.L., Huang, L.J., Li, X.T., An, Q., Geng, L., 2018. Interactive effects of cyclic oxidation and structural evolution for Ti-6Al-4V/(TiC + TiB) alloy composites at elevated temperatures. *Journal of Alloys and Compounds* 752 (5), 164–178.
- Xiang, J., Han, Y.F., Huang, G.F., *et al.*, 2019a. Microstructural evolution in titanium matrix composites processed by multi-pass equal-channel angular pressing. *Journal of Materials Science* 54 (10), 7931–7942.
- Xiang, Y.Y., Wang, X.J., Hu, X.S., *et al.*, 2019b. Achieving ultra-high strengthening and toughening efficiency in carbon nanotubes/magnesium composites via constructing micro-nano layered structure. *Composites Part A: Applied Science and Manufacturing* 119, 225–234.
- Xu, L., Chen, X., Pan, W., *et al.*, 2007. Electrostatic-assembly carbon nanotube-implanted copper composite spheres. *Nanotechnology* 18 (43), 435607.
- Xu, R., Tan, Z.Q., Xiong, D.B., *et al.*, 2017. Balanced strength and ductility in CNT/Al composites achieved by flake powder metallurgy via shift-speed ball milling. *Composites Part A: Applied Science and Manufacturing* 96, 57–66.
- Yang, J.H., Xiao, S.L., Chen, Y.Y., *et al.*, 2020. Microstructure evolution during forging deformation of $(\text{TiB} + \text{TiC} + \text{Y}_2\text{O}_3)/\alpha\text{-Ti}$ composite: drx and globularization behavior. *Journal of Alloys and Compounds* 827, 154170.
- Yang, M., Weng, L., Zhu, H.X., *et al.*, 2017. Simultaneously enhancing the strength, ductility and conductivity of copper matrix composites with graphene nanoribbons. *Carbon* 118, 250–260.
- Yang, X.D., Shi, C.S., He, C.N., *et al.*, 2011. Synthesis of uniformly dispersed carbon nanotube reinforcement in Al powder for preparing reinforced Al composites. *Composites Part A: Applied Science and Manufacturing* 42 (11), 1833–1839.

- Yang, X.D., Liu, E.Z., Shi, C.S., *et al.*, 2013. Fabrication of carbon nanotube reinforced Al composites with well-balanced strength and ductility. *Journal of Alloys and Compounds* 563, 216–220.
- Yang, Z.Y., Wang, L.D., Shi, Z.D., *et al.*, 2018. Preparation mechanism of hierarchical layered structure of graphene/copper composite with ultrahigh tensile strength. *Carbon* 127, 329–339.
- Yoo, S.J., Han, S.H., Kim, W.J., 2012. Magnesium matrix composites fabricated by using accumulative roll bonding of magnesium sheets coated with carbon-nanotube-containing aluminium powders. *Scripta Materialia* 67 (2), 129–132.
- Zhang, L., Wang, Q.D., Liao, W.J., *et al.*, 2017a. Effects of cyclic extrusion and compression on the microstructure and mechanical properties of AZ91D magnesium composites reinforced by SiC nanoparticles. *Materials Characterization* 126, 17–27.
- Zhang, L., Wang, Q.D., Liao, W.J., *et al.*, 2017b. Microstructure and mechanical properties of the carbon nanotubes reinforced AZ91D magnesium matrix composites processed by cyclic extrusion and compression. *Materials Science and Engineering A* 689, 427–434.
- Zhang, X., Shi, C.S., Liu, E.Z., *et al.*, 2017c. In-situ space-confined synthesis of well-dispersed three-dimensional graphene/carbon nanotube hybrid reinforced copper nanocomposites with balanced strength and ductility. *Composites Part A: Applied Science and Manufacturing* 103, 178–187.
- Zhang, X., Zhao, N.Q., He, C.N., 2020. The superior mechanical and physical properties of nanocarbon reinforced bulk composites achieved by architecture design—a review. *Progress in Materials Science* 113, 100672.
- Zhilyaev, A., Langdon, T., 2008. Using high-pressure torsion for metal processing: Fundamentals and applications. *Progress in Materials Science* 53 (6), 893–979.
- Zhou, M.Y., Ren, L.B., Fan, L.L., *et al.*, 2019. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. *Materials Science and Engineering A* 768 (19), 138447.

Two Phase Processing of Metal Matrix Composites

Penchal Reddy Matli, National University of Singapore, Singapore

Tirumalai Srivatsan, The University of Akron, Akron, OH, United States

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

A composite material is a combination of two or more insoluble components having different chemical composition and often various shape. [Mazumdar \(2010\)](#) The continuous phase is referred to as the matrix while the discontinuous phase is referred to as the reinforcement. These two independent components often have noticeable differences in their properties spanning mechanical, physical, electrical and even chemical. One of the components, often the matrix, will be tough and ductile while the other component, namely the reinforcing phase will be light, strong and hard and intrinsically brittle. The metal matrix is often a pure metal or its alloy counterpart and is the continuous phase while the reinforcing phase can be (1) discontinuous in the form of particulates (i.e., particles), short fibers and whisker, and (2) continuous in the form of fibers. This is shown in [Fig. 1](#).

The primary and most desirable need is for the metal matrix composites (MMCs) to offer a healthy combination of properties to include low density, high or adequate strength both in tension and in compression, good thermal expansion characteristics, acceptable creep resistance, good resistance to friction, and overall good wear behavior. ([Ozben et al., 2008](#); [Verma et al., 2017](#); [Sri Ram Murthy and Seetha Rama Rao, 2019](#)) The challenges arising from material design, cost-effective processing, characterization and matrix-reinforcement interfacial characteristics have been systematically addressed for the family of metal matrix composites [MMCs] by several researchers in their independent studies in the time period spanning the last four decades [1980–2020]. Sustained research and development efforts did eventually result in the development and emergence of particulate-reinforced metal matrix composites (MMCs) as potentially viable and an economically affordable option for the purpose of selection and use in a spectrum of applications spanning the fields of military, aerospace, electronics, ground transportation, infrastructure-related industry and high-performance end products. ([Miracle, 2005](#); [Gurusamy et al., 2015](#); [Hassan and Gupta, 2007](#)) Noticeable advances in the domains specific to compositional design commensurate with application have been made possible through sustained research and development efforts.

The ability of relatively inexpensive reinforcements coupled with advances and emergence of processing and fabrication techniques that can result in reproducible microstructures that offer consistent properties spanning the domains of mechanical, physical, electrical and chemical has engineered considerable scientific and technological interest in the selection and use of metal matrix composites (MMCs) for a wide spectrum of applications in the industries spanning automotive, aerospace and few structural end products. The need for reduced structural weight for both aerospace-related applications and automotive applications can be achieved by either increasing the elastic modulus of the engineered composite or by reducing density of the matrix and thus the resultant composite. [Degischer et al. \(1996\)](#) However, the resultant metal matrix composites (MMCs) tend to offer a few observable disadvantages when compared one-on-one with the monolithic counterpart, i.e., pure metal, to include the huge cost arising from processing, inadequate experience, coupled with an overall intrinsically complex processing and fabrication technique(s).

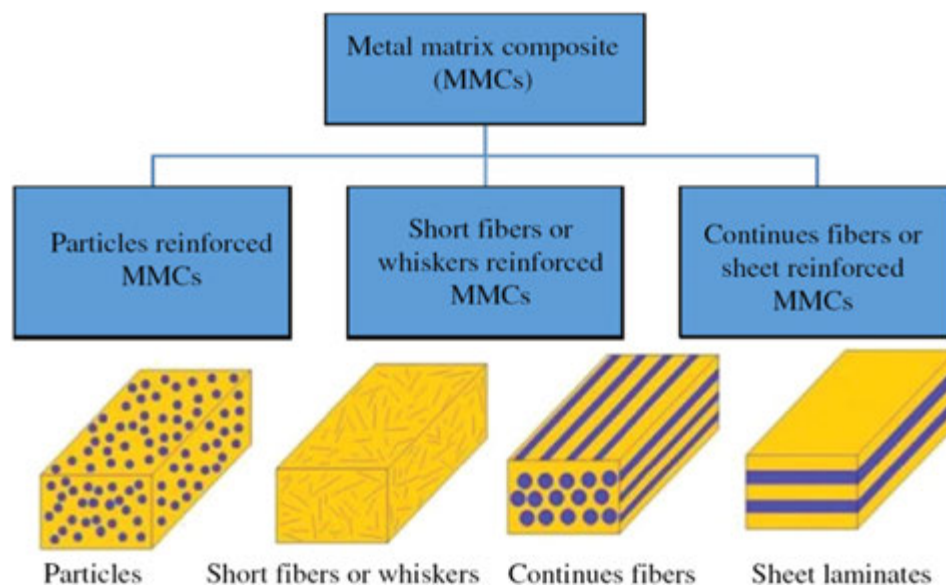


Fig. 1 Classification of metal matrix composites.

The properties to include specific strength (σ/ρ), elastic modulus, rigidity, corrosion resistance, wear resistance and thermal conductivity (Zhang *et al.*, 1993; Sastry *et al.*, 2001) have been noticeably enhanced by the engineering, or synthesis, of metal matrix composites [MMCs] that essentially comprises of a pure metal matrix, or an alloy, that is reinforced with ceramic, organic or metallic compounds. In the synthesis and fabrication of metal-matrix composites [MMCs], spanning both the aluminum-based (Al) composite and magnesium-based (Mg) composite have been given the highest priority when compared to other metals to include titanium (Ti), copper (Cu), nickel (Ni) and iron (Fe). The most prominent characteristics offered by the aluminum-based and magnesium-based metal matrix composites did gain noticeable attention when compared one-on-one with the other alloy-based composites. (Bhoi *et al.*, 2020; Samal *et al.*, 2020; Tjong and Ma, 2000; Gupta and Wong, 2015) Besides, preferential selection and use of the metal-matrix composites [MMCs] in the automotive industry was gradually reduced due essentially because of its low ductility, inadequate fracture toughness, inferior fracture resistance coupled with inferior corrosion resistance upon exposure to environments spanning a range of aggressiveness.

The characteristics specific to high performance and light weight did make the alloys of aluminum and magnesium to be chosen for use as the matrix material in developing composites for a spectrum of applications spanning the industries of automobile and aerospace. Macke *et al.* (2014) The most significant properties, such as good resistance to corrosion and good resistance to wear coupled with low density, high specific strength (σ/ρ) and high specific stiffness (E/ρ) were often exhibited by both monolithic aluminum and magnesium and their alloy counterparts. By systematically varying the size, nature and volume fraction of the reinforcing phase, it was possible to obtain the desired combination of properties for a specific application. Since then both aluminum-based MMCs and magnesium-based MMCs have been preferentially chosen and used for the manufacturing of both aerospace components and automobile components. In the aerospace industry the composites have been chosen for use in fuselage and wings while in the automobile industry the engineered metal-matrix composites have been preferentially chosen for disks, brakes, drums, and pistons. In several cases, the pure metal was often replaced by the alloy counterpart for the metal matrix.

The viable options for producing metal matrix composites [MMCs] were the following techniques: (1) stir casting, (2) mechanical alloying, and (3) powder metallurgy. (Kala *et al.*, 2014; Jayalakshmi *et al.*, 2013). The reinforcing particles often tend to undergo clustering or aggregation, poor interfacial interactions between the soft and ductile metal matrix and the hard and brittle reinforcement coupled with complex manufacturing-related problems that often occur during the conventional manufacturing processes used for the synthesis of the desired metal-matrix composite [MMC]. This often results in reduced, or degraded, mechanical performance of the as-synthesized metal-matrix composite (MMC). (Li *et al.*, 2016; Azamiya *et al.*, 2015) In an attempt to overcome problems specific and related to processing, the technique of spray processing has often been chosen and used as a potentially viable and attractive method for the synthesis of metal matrix composites [MMCs]. The two external powder injectors placed around the melt atomizing section aids in placing the reinforcing particles well within the spray cone during processing. Both clustering and aggregation of the reinforcing particles can be successfully prevented with the help of rapid solidification of the atomized droplets. Ye and Liu (2004).

To eliminate several of these problems and to concurrently increase the ability of a metal matrix composite [MMC] to be synthesized with ease a two-phase process is chosen. This includes the techniques of: (1) spray atomization and deposition processing, and (2) rheocasting. The objective of this article is to examine the key factors that affect and/or exert an influence on two-phase processing, resultant microstructure of the as-synthesized composite and the conjoint influence of processing and microstructure on mechanical behavior of both the aluminum-based composite and the magnesium-based metal matrix composite.

Manufacturing of Metal Matrix Composites

Final properties of the as-synthesized metal matrix composites [MMCs] are often decided and/or dictated by the processing technique that is chosen and used for the specific composite. Olszówka-Myalska *et al.* (2001) For a comprehensive evaluation of the MMCs, a few techniques have been researched upon and progressively developed during the past few decades [i.e., 1980-present] very much in conformance with the prevailing trend. The processing techniques were subsequently classified based entirely on temperature of the metal matrix during processing. Kandpal *et al.* (2014) The processing and resultant fabrication of metal-matrix composites [MMCs] at both the experimental stage and industrial or commercial stage can be broadly classified into the following five stages:

- (1) Liquid phase processes.
- (2) Solid phase processes.
- (3) Deposition techniques.
- (4) In situ processes, and
- (5) Two phase (solid-liquid) processes.

In liquid phase processing, through the use of different proprietary methods the reinforcing particles are gradually added to the molten metal matrix, and the resultant mixture is then allowed to undergo gradual mixing. This culminates with the resultant composite mixture being gradually poured to get components having a definite shape or billets. The billets are subjected to subsequent fabrication with the purpose of getting the desired end product. The techniques of squeeze casting, spray decomposition processing, and liquid metal infiltration, are the three most widely preferred and used liquid phase processing techniques.

In solid phase processing, the blended mixture of elemental powders and reinforcing particulates results in the development of particulate-reinforced metal matrix composite [MMC]. Prior to final consolidation of the blended mixture, few to several measures are often taken to ensure overall success of this processing technique. The techniques of (1) high energy high rate forming, (2) diffusion bonding, and (3) powder metallurgy are categorized to be solid phase processing techniques.

In the manufacturing of metal-matrix composites [MMCs] by use of the technique of spray deposition processing often necessitates the need for the reinforcement fillers to be placed within the matrix material, which results in formation of the desired composite. Subsequently, diffusion bonding of the reinforcement with the metal matrix results in a consolidated composite that conforms with the structural shape that is desired. The techniques of: (1) immersion plating, (2) electro-plating, (3) spray forming, and (4) spray decomposition, are some of the widely chosen and used decomposition processes. The technique of in-situ processing is also referred to as reactive processing. In this processing technique, refractory reinforcements are favored to form in an aluminum alloy metal matrix by reaction.

A combination of the hard, brittle and elastically deforming ceramic reinforcement with a soft, ductile and plastically deforming metal matrix was carried out in two-phase processes in the area of the phase diagram where the matrix contains both the liquid phase and the solid phase. Based on this two-phase processing concept, the following three techniques were found to be technically viable and economically affordable and hence the most prominent:

- (1) Spray atomization and deposition.
- (2) Rheocasting.
- (3) Osprey deposition.

Spray Atomization and Deposition Processing

The spray atomization and deposition processing is a semi-liquid synthesis technique that has been preferentially used for the purposes of processing discontinuously-reinforced metal-matrix composite [MMC]. In this specific technique, the metal matrix in the semi-solid state and the desired reinforcement are thoroughly mixed. This processing technique offers several unique properties that vary from solid to liquid and two-phase processing. In this technique, both mixing and consolidation are finished in a single operation, which is by far the most important and key aspect specific to this technique.

The atomizing of matrix material into a fine diffusion of droplets using pressure-controlled inert gas jets that also aids in heating the reinforcing particles during flow through the inlets is shown in Fig. 2. Garg *et al.* (2019).

Srivatsan and Lavernia (1992) have studied and documented the different synthesis techniques using particulate technology and came to the conclusion that the technique of spray deposition processing was one that was potentially viable, economically affordable and an overall attractive manufacturing technique for the production of high quality metal matrix composites [MMCs].

On a chosen surface the reinforcement can be applied upon which the molten metal is then sprayed. By introducing the particulate reinforcement into the metal spray and the resultant mixture is then co-deposited onto the surfaces. Thus, an ingot of the desired metal-matrix composite [MMC] can be produced using the technique of spray deposition processing. A uniform supply of the reinforcing particulates by ensuring careful control of both the atomizing and reinforcement feeding conditions is essential. A few of the manufacturing techniques coupled with essential mechanical property characterization of the as-synthesized MMC was initially studied and put forth by Mistry and Gohil (2017). They came to the conclusion that spray deposition processing did offer a useful

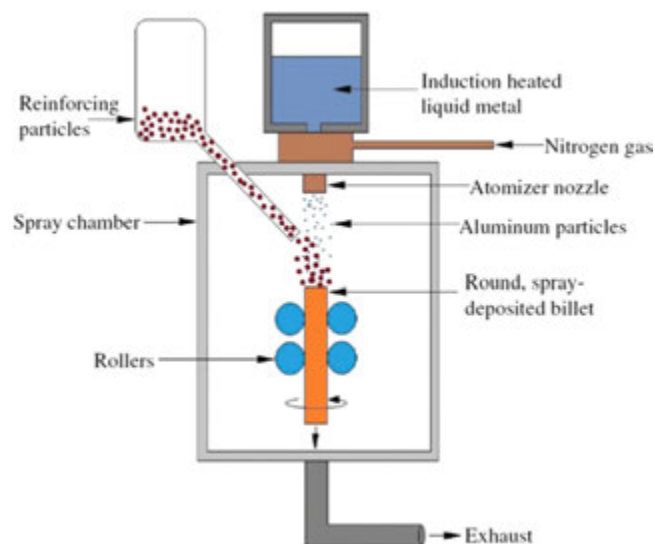


Fig. 2 Spray atomization and deposition of metal-matrix composites. Reproduced from Mistry, J.M., Gohil, P.P., 2017. Research review of diversified reinforcement on aluminium metal matrix composites: Fabrication processes and mechanical characterization. *Science and Engineering of Composite Materials* 25 (4), 1–15.

combination of high production rate and low solidification time. This is particularly advantageous for the synthesis of a metal-matrix composite [MMC] by enabling minimum reaction time of the chosen matrix material with the particulate reinforcement.

Rheocasting Process

In the technique of rheocasting, (Arunachalam *et al.*, 2019) a semi solid slurry is developed from the molten alloy through shearing action and the reinforcement particles are often trapped during the solidification process. To ensure shaping of the desired component, the resultant slurry is often transferred to a die. The key aspects specific to the technique of rheocasting are the following: (1) in-house scrap, (2) energy saving recycling, and (3) feed stock like special solid billet, which is often required for the technique of thixocasting. Due to a healthy combination of overall cost effectiveness coupled with high productivity for manufacturing of the semi-solid metal (SSM), (Elsharkawi *et al.*, 2014) this processing technique has stood out to be the most prominent fabrication technique during recent years. By applying pressure on the chosen reinforcement often results in an excellent microstructure coupled with highly localized intensive shearing that contributes in an observable way to enhancing distribution of the reinforcing particles in the chosen metal matrix of the as-synthesized metal-matrix composite [MMC]. Ostad Shabani *et al.* (2016) By a careful addition of the reinforcing particles to the partially solid alloy, it is possible to prevent both the settling and agglomeration of the reinforcing particles by this technique.

The reinforcement should not only be constant at a specific temperature but also non-reactive during the entire rheocasting process. Silicon carbide (SiC) and aluminum oxide (Al_2O_3) were the two most common reinforcements that have been chosen for reinforcing metal matrices. A systematic diagram of this process is shown in Fig. 3. Curle and Ivanchev (2010) The primary advantages of this technique are a high-quality cast component of the as-processed, or as-synthesized, metal matrix composite, to include the following:

- (1) Free of porosity,
- (2) Complex parts,
- (3) Excellent filling of the metal,
- (4) Acceptable mechanical performance,
- (5) Reduced shrinkage, and
- (6) Good surface finish.

When compared one-on-one with the other methods of casting, the wear property of the Rheosqueeze cast metal matrix composite [MMC] is noticeably evident. The primary disadvantage with this technique is that it necessitates the need for advanced technology for the purpose of production, which requires that the desired operators be both aware and knowledgeable of the intricacies specific to advanced technology while concurrently exposing themselves to adequate training. Very little work has been done with this processing technique and up until now no effective and extensive materials characterization data can be found in the published literature. (Flemings *et al.*, 1976; Poddar *et al.*, 2009; Rahimi *et al.*, 2015).

Curie *et al.* (Curle and Ivanchev, 2010) manufactured silicon carbide reinforced cast aluminum alloy AA359-based composites using the technique of rheocast processing. They observed the hardness of the as-synthesized composite to increase from 73 HRB to 93 HRB for an increase in silicon carbide (SiC) reinforcement content by as much as 11 vol%.

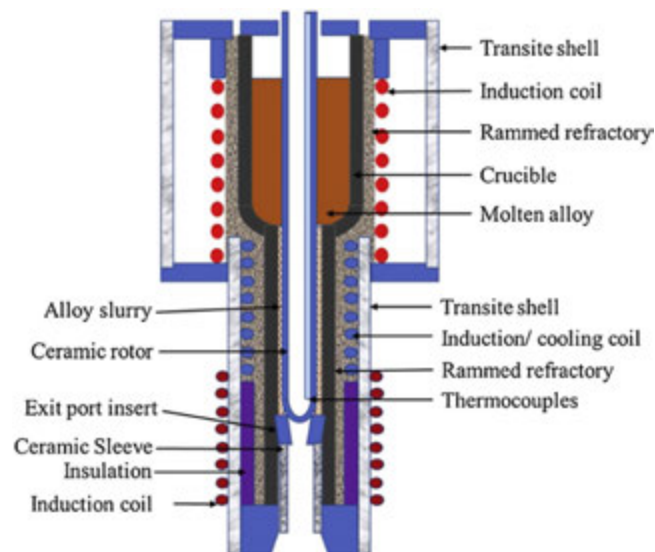


Fig. 3 Schematic showing apparatus for the Rheocasting of metal matrix composites. Reproduced from Arunachalam, R., Krishnan, P.K., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *Journal of Manufacturing Processes* 42, 213–245.

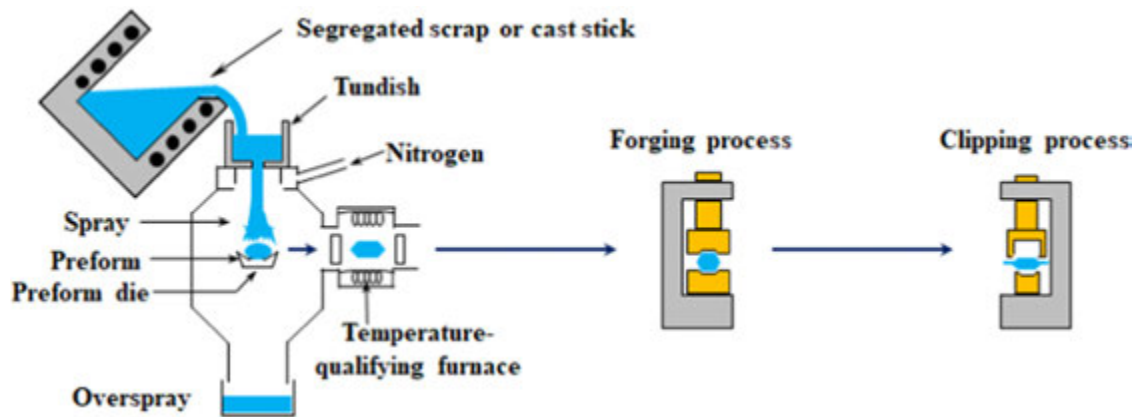


Fig. 4 A schematic of the modified Osprey technique.

The Osprey Deposition Process

In the Osprey deposition process, the reinforcing particulates are in touch with the molten alloy and the resultant mixture is carefully atomized using inert gas jets during synthesis of the metal-matrix composite. [Leatham et al. \(1990\)](#) This is shown in [Fig. 4](#).

In the form of reinforced metal matrix billets, the final sprayed mixture is collected on the surface. The Canadian aluminum company [ALCAN] was the first to introduce this method as an extrapolation of the Osprey process. [White et al. \(1988\)](#) This processing technique was essentially a combination of both blending and consolidation steps specific to the powder metallurgy process. This has made possible observable strides in the synthesis, development and emergence of metal-matrix composites [MMCs].

The Osprey deposition is a typical two-phase processing technique that has found for itself selection and use for both high performance-critical and low performance-critical applications. Through the spray jets of inert gas, the reinforcing particulates are injected and atomized to the substrate of the molten-metal or alloy matrix. The resultant solid mixture is then held onto a non-wetting surface. Recent studies have convincingly shown that the spray atomized products are essentially free of microscopic segregation while concurrently possessing fewer gas content. Besides, they are capable of having certain characteristics, which can be related to rapid solidification processing. Extruded billets of an aluminum-silicon alloy ([Ejiofor and Reddy, 1997](#)) having noticeably good to outstanding dimensional tolerance have been easily fabricated using the technique of Osprey deposition.

Properties of Metal Matrix Composites [MMCs] Produced Using Various Two-Phase Processes

A proper selection of the variables to include the following: (1) reinforcement, (2) processing technique chosen, (3) parameters specific to the processing technique, and (4) matrix of the as-synthesized metal matrix composite [MMC] does help in engineering improvements in the overall quality of the engineered metal-matrix composite [MMC]. The parameter can in fact either be modified or tailored to suit a particular application.

[Chaorun et al. \(Si et al., 2017\)](#) produced silicon carbide particulate [SiC_p] reinforced aluminum alloy 7075-based composites using the technique of spray atomization and deposition processing. In an attempt to evaluate the proposed technique, the microstructure and mechanical behavior of test specimens of the as-synthesized composite were compared one-on-one with the conventional spray formed aluminum alloy 7055. Microstructure of the as-synthesized aluminum alloy 7055 - SiC_p metal-matrix composite [MMC] had near equiaxed shaped grains with an overall fine structure. This is evident in the optical micrographs shown in [Fig. 5\(a\)](#). As seen in [Fig. 5\(b\)](#), under identical atomizing conditions the microstructure of the as-synthesized aluminum alloy 7055/SiC_p composite had grains with an average size of 16 μm, which was noticeably smaller than that of the spray formed aluminum alloy 7055 counter-part (about 24 μm).

An observable improvement in mechanical properties of the spray formed or spray processed composite, i.e., MMC, due to the refined grain size, has been both observed and recorded in an earlier study. [Liu et al. \(2016\)](#) A schematic of the spray deposition processing technique along with optical micrographs of the as-synthesized aluminum alloy based metal matrix composite are shown in [Fig. 6](#).

The XRD curves and the strain versus stress response in compression for the 7055-SiC_p composite and the unreinforced counterpart, i.e., aluminum alloy 7055, at room temperature [27°C], are shown in [Fig. 7](#). The second precipitate phase that was present in the microstructure was the η phase (MgZn₂). This is evident for the 7055-SiC_p composite from the X-ray diffraction (XRD) curves shown in [Fig. 7\(b\)](#). A nominal increase of 4.64% for the compression peak strength i.e., 687.5 MPa, was observed for the 7055-SiC_p composite when compared one-on-one with the spray formed aluminum alloy 7055. This is clearly shown in [Fig. 7\(a\)](#). Further, this provides convincing evidence for two-phase atomization and deposition processing to be safely considered as one of the most prominent processing techniques proposed for the family of metal matrix composites [MMCs].

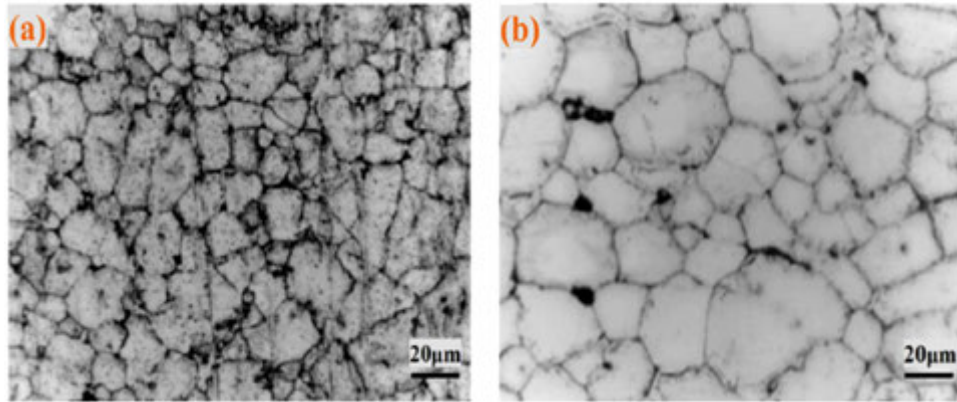


Fig. 5 Optical micrographs showing grain structure of (a) 7055-SiCp composites, and (b) Spray formed 7055Al alloy.

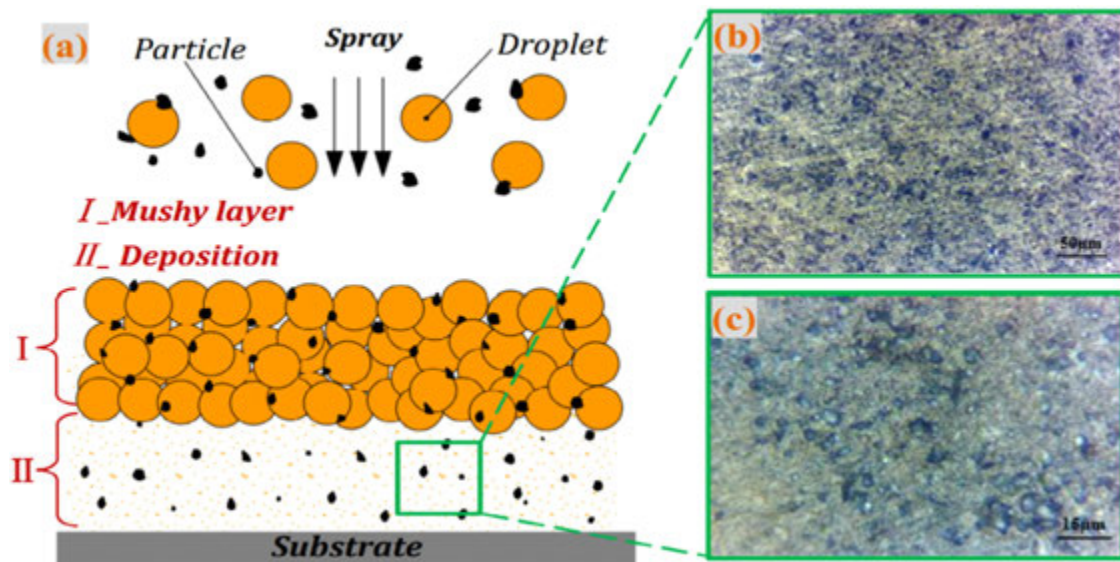


Fig. 6 (a) A schematic of the spray deposition process. (b) Optical micrographs showing microstructure of the as-synthesized 7055-SiCp composite, and (c) High magnification observation of (b).

The observed enhancement in mechanical properties of the as-synthesized 7055/SiCp composite when compared one-on-one with the spray formed 7055 aluminum alloy counterpart can be attributed to the conjoint and mutually interactive influences of the following:

- (1) A decrease in grain size of the 7055 SiCp composite as a direct consequence of atomization resulting in fine grain strengthening.
- (2) A near uniform distribution of the reinforcing silicon carbide (SiC) particles through the aluminum alloy metal matrix that ensures noticeable contribution from particle strengthening.
- (3) During phase atomization and deposition processing a rapid solidification of the alloying elements does result in a super saturated solid solution (SSSS) and the resultant strengthening from the solid solution.

Yang *et al.* (2019) did conduct an exhaustive study of the Al7055/SiC_p composites using the technique of spray deposition. The volume fraction of the reinforcing silicon carbide particles (SiC_p) in the aluminum alloy metal matrix was 17%. The effect of SiC_p on both microstructural development and resultant mechanical properties of the as-synthesized composite was carefully examined. In this independent study, the spray-deposited AA7055/SiC_p metal matrix composite was composed of alpha-aluminum, silicon carbide particulates (SiC_p), and the precipitates Al₂CuMg, Al₂Cu and MgZn₂. Size of the liquid particles of aluminum are noticeably different, and the phenomenon of large particles consuming the small particles was common in areas containing a high volume fraction of the reinforcing SiC particles. This is essentially because of a synchronization of the nucleation kinetics caused by noticeable differences in cooling rates of the hard and brittle reinforcing SiC particles and the soft and ductile aluminum alloy

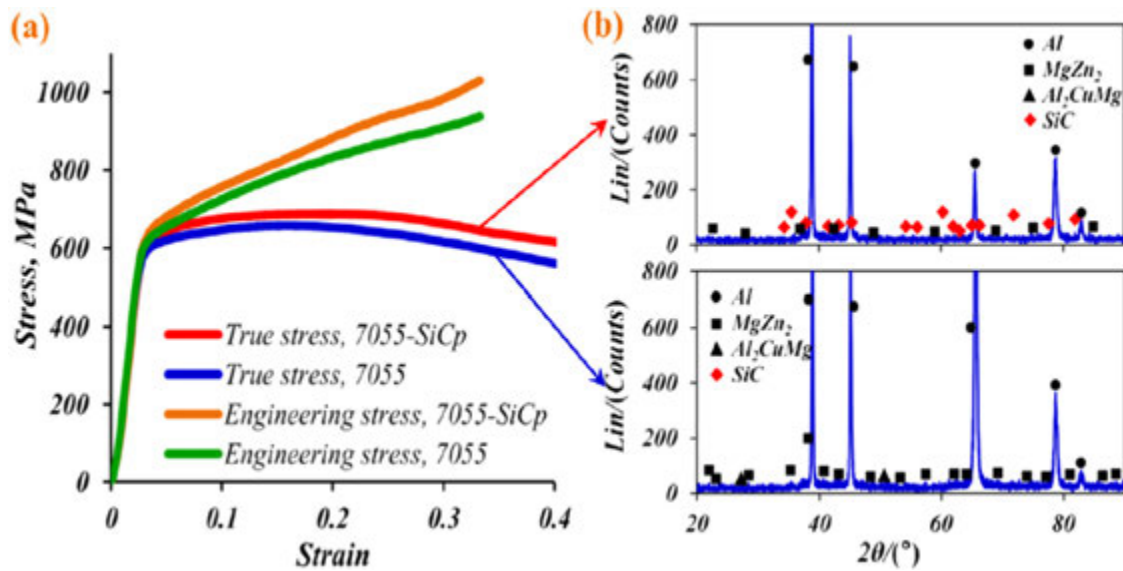


Fig. 7 (a) Stress-strain curves and X-ray diffraction patterns (XRD) for both the aluminum alloy 7055-SiCp composite and aluminum alloy 7055. (b) X-ray diffraction patterns of the as-synthesized 7055-SiCp composite and the unreinforced aluminum alloy 7055.

metal matrix. The silicon and carbon present on the surface of the reinforcing SiC_p tend to gradually diffuse into the aluminum metal matrix. A distribution of these two key elements, i.e., carbon and silicon, followed by a pattern of gradual weakening of the reinforcing SiC particles (SiC_p) results in the formation of a ring-shaped zone that is enriched in both carbon and silicon around the reinforcing SiC particles. The presence of two phases, i.e., AlCu and AlMgCu, in the as-synthesized composite was detected both at and along the boundaries of the liquid aluminum particle, but also on the surface of the reinforcing silicon carbide (SiC) particles. These particles or phases tend to gradually grow both at and along the edges and corners of the reinforcing SiC_p. The reinforcing silicon carbide (SiC) particles tend to hinder or prevent propagation of both the tear edges and fine microscopic cracks. The tear edges and fine microscopic cracks will tend to gradually propagate around the reinforcing SiC particles (SiC_p). This contributes in a small way to increasing their propagation path while concurrently contributing to delaying failure of the material by fracture. Conventionally, a high temperature is maintained during the deposition processes. Subsequent to atomization, droplets of aluminum alloy 7055 will tend to react with the reinforcing silicon carbide particles (SiC_p). The gradient region of silicon and carbon was gradually dissolved from surface of the reinforcing SiC particle (SiC_p). This can be seen from the EDS midline scanning that is shown in Fig. 8.

Mechanical properties of the aluminum alloy metal-matrix composites in the radial direction were found to be better than those in the longitudinal direction. The tensile strength and elongation following fracture was 17.4% and 8% higher in the radial direction when compared to the longitudinal direction. Fracture morphology of the chosen aluminum alloy based metal matrix composite essentially revealed a combination of cleavage and pockets of dimples, with few features reminiscent of “locally” brittle fracture.

Esmaily *et al.* (2016) fabricated SiC particle-reinforced AM50 matrix composite and AZ91D matrix composite using the technique of RheoMetal process by investigating the newly developed and emerging technique of rheocasting (RC). The microstructure and hardness of the as-synthesized magnesium-based metal matrix composites [MMCs] was examined and compared one-on-one with the unreinforced counterpart.

In this study, the researchers used two separate experiments to examine the effect of rheocasting process on microstructure of the rheocast magnesium alloy AM50-based MMC and AZ91D-based MMC. In the first experiment, they fabricated SiC particle-reinforced magnesium-based MMCs to examine the formation, presence and distribution of the different intermetallic particles through the microstructure during solidification. In the second experiment, by quantitatively analysing the microstructure of the as-synthesized metal-matrix composites (MMCs), they were able to systematically investigate the magnesium alloy-based MMCs for different volume fractions of the particulate reinforcement. They found the reinforcing SiC particles to be distributed uniformly through the microstructure. Use of image analysis technique helped in differentiating the parent alloy with specific reference to both defects created during casting and the resultant microstructure.

The fabrication of rheocast AZ91-based and rheocast AZ50-based MMC is shown in Fig. 9. The molten metal was converted into slurry using internal enthalpy exchange material (EEM) that is needed for the Rheocast process.

The resultant metal matrix composite (MMC) was fabricated from the RheoMetal that was placed between two liquid metals at a comparatively low super heat and the solid metal attached to a stirrer. The rod tends to cool to a normal temperature upon immersion in the melt. In this method, the melt was cooled noticeably faster than melting of the enthalpy exchange material (EEM) and a homogeneous slurry was ensured during processing. The two magnesium alloys that were chosen as matrices were:

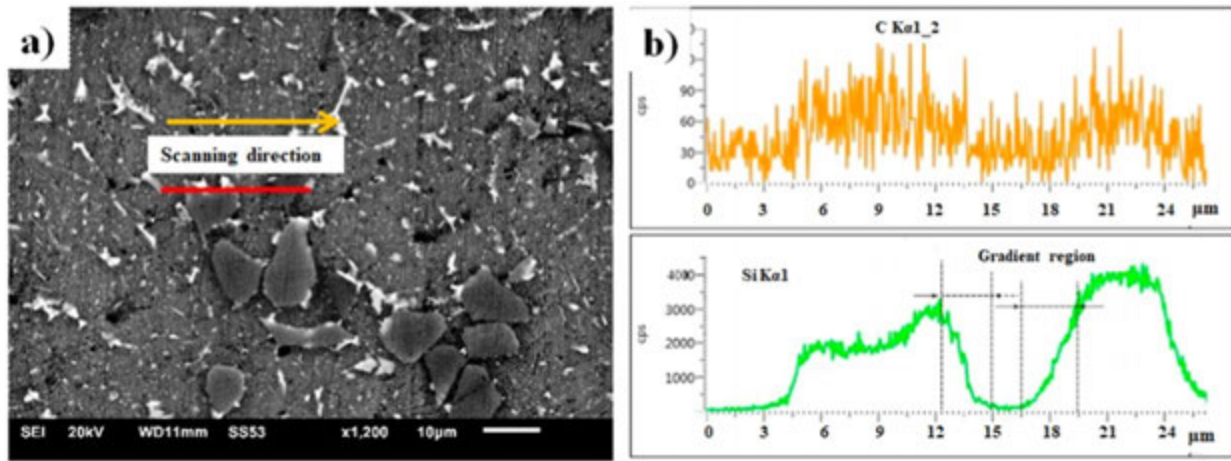


Fig. 8 (a) The line scanning image, and (b) Distribution of the elements carbon (C) and silicon (S) along the scan line in (a) of spray-deposited AA7055/SiCp metal matrix composites.

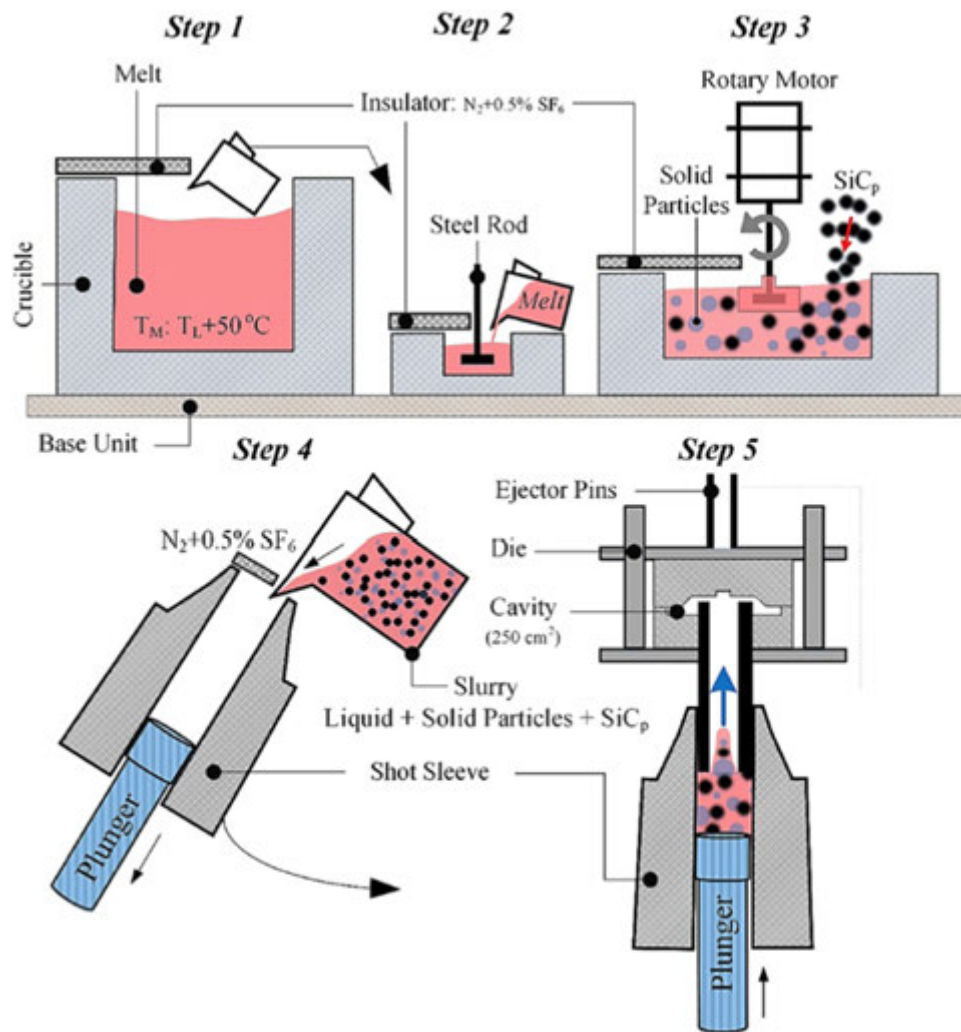


Fig. 9 A schematic of the rheocast (RC) process used for the fabrication of magnesium-alloy based metal matrix composites.

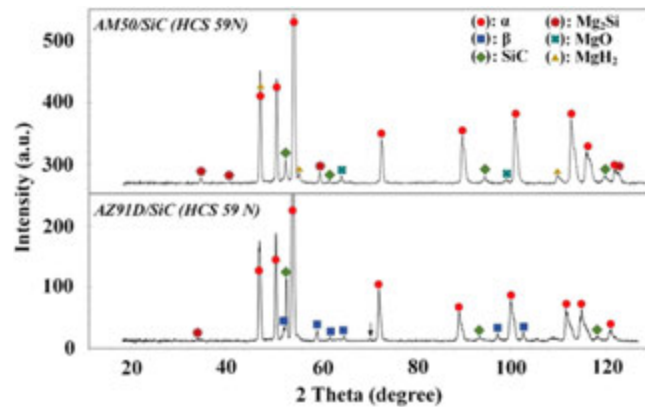


Fig. 10 X-ray diffraction (XRD) diffractograms of RC AM50 and AZ91D reinforced with silicon carbide (SiC) particles.

(1) AM50, and (2) AZ91D. Further, two different sizes of the reinforcing SiC particles (SiC_p) were used for the purpose of manufacture of the desired metal matrix composite. The first experiment involved reinforcing the SiC particles (SiC_p), ranging in size from 0.1 μm to 0.9 μm (HCS 59N), with magnesium alloy AZ91D. In the second experiment for magnesium alloy AM50 the reinforcing SiC particles (SiC_p) varied in size from 4 to 28 μm (HCS 400).

The X-ray diffraction patterns for the rheocast AZ91 MMC and rheocast AM50-based MMC are shown in **Fig. 10**. With specific reference to α -Mg, the β -phase ($\text{Mg}_{17}\text{Al}_{12}$) had a comparatively low intensity peak for the two chosen composites. These peaks could be easily detected for the AZ91D alloy while it was difficult to detect for the AM50 alloy. The β -SiC had strong peaks for the two chosen magnesium alloys. When compared to magnesium alloy AZ91D, the peaks related to the intermetallic particles MgO and Mg_2Si had better, clear and sharp intensity.

For both the magnesium alloy-based metal matrix composites [MMCs], a few of the peaks had properties that were similar to magnesium Hydride (MgH_2).

The microstructure of magnesium alloy AM50 and magnesium alloy AZ91D reinforced with SiC particles (HCS 59N) is as shown in **Fig. 11**. The SiC particulate clusters were seen in both the AM50 alloy and AZ91D alloy, which can be inferred from the scanning electron microscopy images. A few noticeable changes in the grain structure was observed for the SiC particle reinforced AM50-based metal matrix composite [MMC].

For the AM50 alloy-based composite, an observable decrease in the grain size of α -Mg, by as much as 28-mm, was observed. Furthermore, an increase in aspect ratio of ~ 0.8 was observed for the α -Mg grains that was made possible by the addition of the reinforcing SiC particles. This clearly demonstrates a noticeable enhancement in the spherical morphology of the primary α -Mg grains. In the inter dendritic regions traces of the β -phase particles were observed. Similar observations were recorded for the AZ91D alloy-based MMC.

The intrinsic difference in hardness of the alloys AM50, AZ91D, and the composite counterparts is shown in **Fig. 12**. It is observed that the engineered MMCs were noticeably harder than the host alloy. Due to the presence of clusters of the reinforcing SiC particulate (SiC_p) in the as-synthesized MMCs an observable difference in the hardness values was noted. The hardness value of alloy AM50 and alloy AZ91D were increased to a maximum value in the range of ~ 50 to 73 and ~ 64 to 76 with the use of HCS 59N particulate reinforcement. The HCS 400 particulate reinforcement revealed lower hardness than HCS 59N, which incidentally is noticeably harder than the unreinforced rheocast alloys AM50 and AZ91D.

Poddar *et al.* (2009) studied the mechanical properties and microstructure characteristics of SiC particle- reinforced magnesium-based composite synthesized using the technique of rheocasting. A temperature of 596°C and 468°C was applied to both the liquidus and solidus states in this independent research study. The magnesium ingot pieces were placed in a mild steel crucible that was coated with boron nitride kept in a resistance furnace during the initial stages. Prior to charging the crucible, the raw materials were preheated at 250°C. The furnace temperature was then increased to 750°C for 30 min. At this temperature the melt was kept for the purpose of ensuring complete homogenization. During stirring, the preheated SiC particles (SiC_p) were gradually added to the alloy slurry. Using a rotational speed of 450 rpm and maintaining a temperature of $584 \pm 2^\circ\text{C}$, the melt was gradually stirred with the help of a mechanical stirrer for full 20 min during the rheocasting process. Subsequently, the slurry was filled into rectangular molds that measured 20 mm $\times$ 100 mm $\times$ 300 mm. The resultant ingots of both the rheocast alloy and the composite counterpart were heat treated at a temperature of 415°C for 18 h in an environment of carbon dioxide gas.

These researchers also reported the SiC particles (SiC_p) to be uniformly distributed in the matrix of the rheocast AZ91D alloy. The fine size of the reinforcing SiC particles did result in their agglomeration in the as-synthesized AZ91D/15 SiC_p composite. The growth of primary α -Mg grains forced the reinforcing particles to the grain boundary regions and their small size was conducive for both clustering and agglomeration. The clustering and agglomeration of the reinforcing SiC particles at the boundary regions was essentially because of the high surface tension force due to the high volume ratio at the region of the interface.

The values of hardness of the as-cast composites are summarized in **Table 1**. When compared to the unreinforced counterpart, the composite samples did possess noticeably higher hardness. The hard and brittle reinforcing SiC particles (SiC_p) tend to suppress matrix

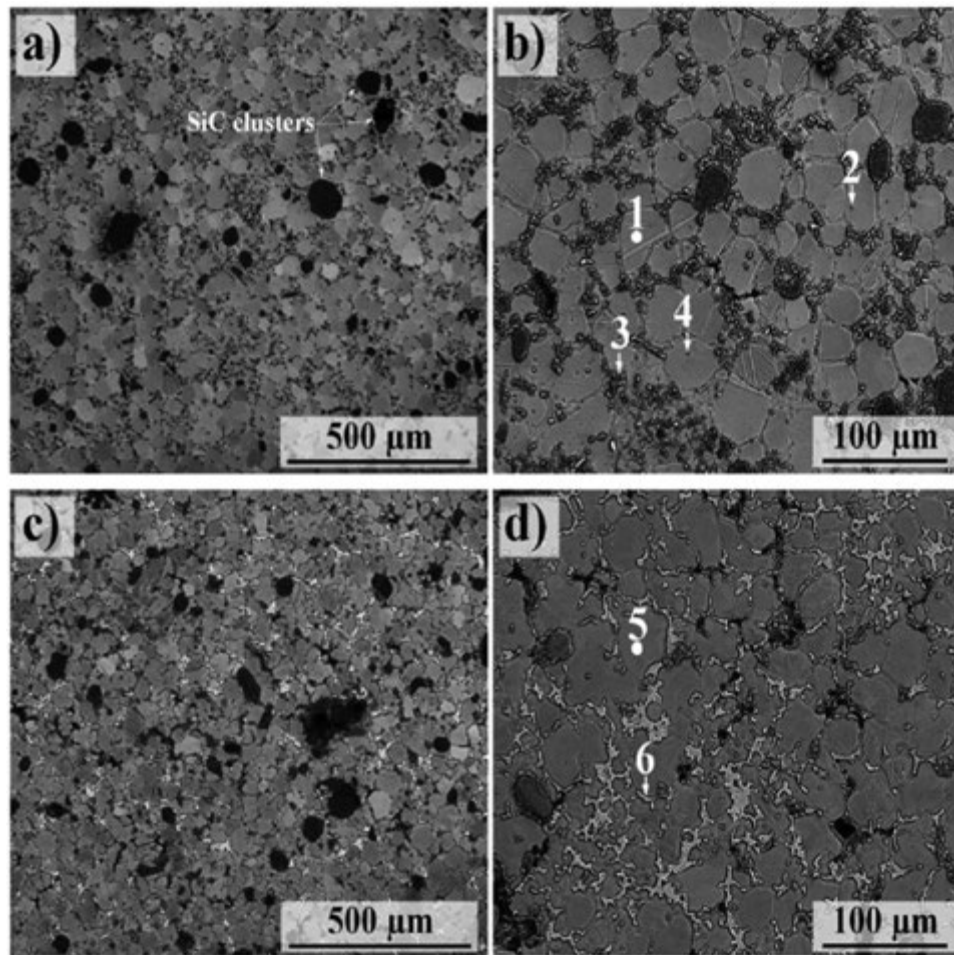


Fig. 11 Scanning electron micrographs of rheocast magnesium-based MMC, (a) and (b) AM50 alloy-based metal-matrix composite (MMC), (c) and (d) AZ91 alloy-based metal matrix composite (MMC).

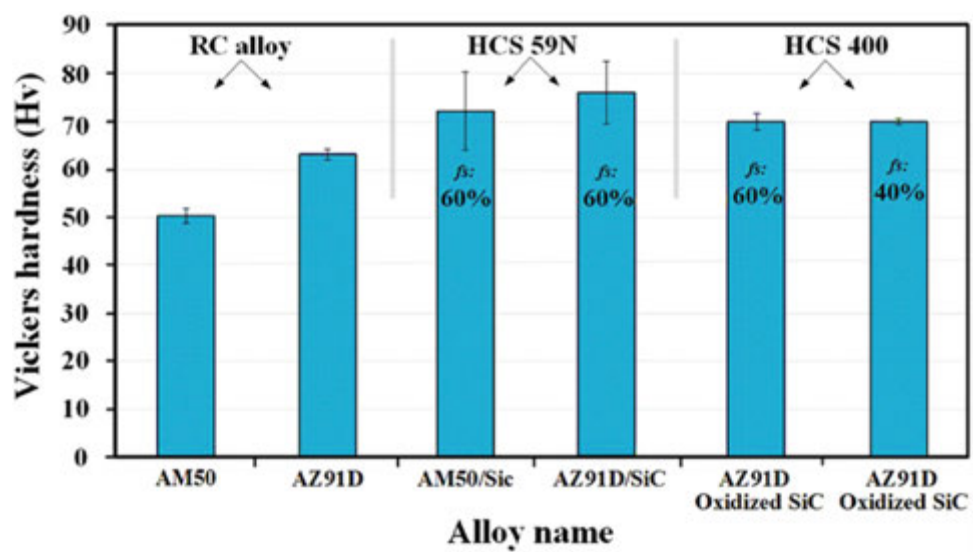


Fig. 12 Hardness of Rheocast alloys and the resultant metal matrix composites [MMCs].

Table 1 Results of hardness measurement on both the As-cast and T4 heat-treated specimens

Material	Condition	Particle size (μm)	Microhardness (HV, 0.5 N)	
			Matrix (± 1)	SiC/matrix interface (± 3)
AZ91D	As cast	–	62	–
AZ91D	T4	–	75	118
AZ91D/15 SiCp	As cast	150	78	106
AZ91D/15 SiCp	T4	150	65	–
AZ91D/15 SiCp	As cast	15	77	93
AZ91D/15 SiCp	T4	15	81	89

deformation by constraining the movement of dislocations. The load bearing capacity of the resultant composite material was enhanced by the presence of the reinforcing silicon carbide particles (SiC_p)s in the microstructure of the engineered composite material. At the particle-matrix interfaces, the micro-hardness value revealed an observable decrease following the T4 heat treatment.

The total elongation for the AZ91D/15 SiC_p (grain size of 150 μm) composite was 1.6% and for the AZ91D/15 SiC_p composite (grain size of 15 μm) it was 1.8%, which is noticeably less than that for the unreinforced alloy (8%). The gradual transfer of load from the soft, ductile and plastically deforming metal matrix to the hard, brittle and essentially elastically deforming particulate reinforcement was the basic mechanism governing deformation of the chosen composite at the fine microscopic level. Enhanced mechanical properties coupled with good load carrying capability could be easily achieved by the good bonding between the reinforcing silicon carbide particles (SiC_p) and the chosen metal matrix.

The Osprey process was developed to prepare both aluminum-based and aluminum alloy based metal matrix composites. [Leatham et al. \(1989\)](#) In this technique, the reinforcement particle was introduced into a stream of the molten alloy. The molten metal is subsequently atomized using a jet of inert gas. The sprayed mixture was allowed to solidify on a substrate resulting in the formation of fine pellets.

A method for manufacturing hypereutectic Al-Si alloys was developed by Osprey Metals Ltd, which was termed as the Osprey deposition process and was based essentially on the technique of spray deposition. The need for both a simple technique and low processing cost was essential since the processing parameters were often complex and the resultant manufacturing cost was noticeably high. An important aspect was the critical need to maintain flow rate of the melt along with the required characteristics for both atomization and deposition. [Cai et al. \(2015\)](#).

Conclusions

This article provides an adequate insight into the two-phase fabrication process coupled with a brief overview of both microstructure and mechanical characteristics of the as-synthesized metal matrix composites [MMCs]. The advantages and limitations of each of the processes are presented and briefly discussed. Choice of the appropriate processing technique is influenced by a variety of factors to include: (1) production cost, (2) process efficiency, (3) quality desired in the product, and (4) end application. A few of the key highlights resulting from this short article are the following:

- (1) Of the several methods for fabrication, spray deposition has now gained the recognition of being the most promising technique for the purpose of development of metal-matrix composites [MMCs] due to a healthy synergism of a technically viable and an economically affordable cost-effective process.
- (2) The metal matrix composites [MMCs] having improved mechanical properties can be successfully produced by an appropriate selection of the processing technique and the associated process parameters to include the following: (1) nature of the metal matrix, (2) type, nature and volume fraction of the reinforcing phase, (3) other additives used, if any, and (4) use of wetting agent.
- (3) The extensive macroscopic segregation that is normally associated with traditional casting processes can be either prevented or minimized by the technique of Spray Atomization and Deposition processing.
- (4) Test samples of the rheocast Mg-SiC composites revealed noticeable improvement in elastic modulus, hardness and yield strength, with a marginal decrease in ductility and ultimate tensile strength.
- (5) Aluminum alloy 7075, which is a preferred candidate for selection and use in structural applications in combination with silicon carbide (SiC) reinforcement finds for itself selection and use in industries spanning the automobile sector and performance-related products.

References

- Arunachalam, R., Krishnan, P.K., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *Journal of Manufacturing Processes* 42, 213–245.
- Azarniya, A., Hosseini, H.R.M., Jafari, M., Bagheri, N., 2015. Thermal decomposition of nanostructured aluminium titanate in an active Al matrix: A novel approach to fabrication of in situ $\text{Al}/\text{Al}_2\text{O}_3\text{-Al}_3\text{Ti}$ composites. *Materials Design* 88, 932–941.

- Bhoi, N.K., Singh, H., Pratap, S., 2020. Developments in the aluminium metal matrix composites reinforced by micro/nano particles – A review. *Journal of Composite Materials* 54 (6), 813–833.
- Cai, Z., Zhang, C., Wang, R., *et al.*, 2015. Preparation of Al-Si alloys by a rapid solidification and powder metallurgy route. *Materials Design* 87, 996–1002.
- Curle, U.A., Ivanchev, L., 2010. Wear of semi-solid rheocast SiCp/Al metal matrix composites. *Transactions of Nonferrous Metals Society of China* 20, s852–s856.
- Degischer, H.P., Schulz, P.A., Lacom, W., 1996. Properties of continuous fibre reinforced Al and Mg-matrix composites produced by gas pressure infiltration. *Key Engineering Materials* 127–131, 99–110.
- Ejiofor, J.U., Reddy, R.G., 1997. Developments in the processing and properties of particulate Al-Si composites. *Journal of Metals* 49 (11), 31–37.
- Elsharkawi, E.A., Pucella, G., Côte, P., Chen, X., 2014. Rheocasting of semi-solid Al359/20% SiC metal matrix composite using SEED process. *Canadian Journal of Metallurgy and Materials Science* 53, 160–168.
- Esmaily, M., Mortazavi, N., Svensson, J.E., *et al.*, 2016. A new semi-solid casting technique for fabricating SiC-reinforced Mg alloys matrix composites. *Composites Part B Engineering* 94, 176–189.
- Flemings, M.C., Riek, R.G., Young, K.P., 1976. Rheocasting. *Materials Science and Engineering* 25, 103–117.
- Garg, P., Jamwal, A., Kumar, D., *et al.*, 2019. Advance research progresses in aluminium matrix composites: Manufacturing and applications. *Journal of Materials Research and Technology* 8 (5), 4924–4939.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–34.
- Gurusamy, P., Prabu, S.B., Paskaramoorthy, R., 2015. Influence of processing temperatures on mechanical properties and microstructure of squeeze cast aluminium alloy composites. *Materials and Manufacturing Processes* 30, 367–373.
- Hassan, S.F., Gupta, M., 2007. Development of high strength magnesium based composites using elemental nickel particulates as reinforcement. *Journal of Materials Science* 37, 2467e74.
- Jayalakshmi, S., Gupta, S., Sankaranarayanan, S., Sahu, S., Gupta, M., 2013. Structural and mechanical properties of Ni60Nb40 amorphous alloy particle reinforced Al-based composites produced by microwave-assisted rapid sintering. *Materials Science and Engineering A* 581, 119–127.
- Kala, H., Mer, K.K.S., Kumar, S., 2014. A review on mechanical and tribological behaviours of stir cast aluminium matrix composites. *Procedia Materials Science* 6, 1951–1960.
- Kandpal, B.C., Kumar, J., Singh, H., 2014. Production technologies of metal matrix composite: A review. *International Journal of Research in Mechanical Engineering & Technology* 4 (2), 27–32.
- Leatham, A., Ogilvy, A., Chesney, P., Wood, J.V., 1989. Osprey process – production flexibility in materials manufacture. *Metal and Materials* 5, 140–143.
- Leatham, A.G., Brooks, R.G., Coombs, J.S., Ogilvy, A.J., 1990. The past, present, and future development of the Osprey preform process. In: *Proceedings of the 1st International Conference on Spray Forming, Osprey Metals, Swansea*.
- Li, S., Su, Y., Ouyang, Q., Zhang, D., 2016. In-situ carbon nanotube-covered silicon carbide particle reinforced aluminium matrix composites fabricated by powder metallurgy. *Materials Letters* 167, 118–121.
- Liu, B., Lei, Q., Xie, L., Wang, M., Li, Z., 2016. Microstructure and mechanical properties of high product of strength and elongation Al-Zn-Mg-Cu-Zr alloys fabricated by spray deposition. *Materials Design* 96, 217–223.
- Macke, A., Schultz, B.F., Rohatgi, P.K., Gupta, N., 2014. Metal matrix composites for automotive applications. In: Elmarakbi, A. (Ed.), *Advanced Composite Materials for Automotive Applications: Structural Integrity and Crashworthiness*. John Wiley & Sons.
- Mazumdar, S.K., 2010. *Composites Manufacturing: Materials, Product, and Process Engineering*. Boca Raton: CRC Press LLC.
- Miracle, D.B., 2005. Metal matrix composites – From science to technological significance. *Composites Science and Technology* 65, 2526–2540.
- Mistry, J.M., Gohil, P.P., 2017. Research review of diversified reinforcement on aluminium metal matrix composites: Fabrication processes and mechanical characterization. *Science and Engineering of Composite Materials* 25 (4), 1–15.
- Olszówka-Myalska, A., Szala, J., Cwajna, J., 2001. Characterization of reinforcement distribution in Al/(Al₂O₃)_p composites obtained from composite powder. *Materials Characterization* 46 (2–3), 189–195.
- Ostad Shabani, M., Heydari, M., Tofigh, A.A., Reza Rahimpour, M., 2016. Wear properties of rheo-squeeze cast aluminium matrix reinforced with nano particulates. *Protection of Metals and Physical Chemistry of Surfaces* 52, 489–491.
- Ozben, T., Kilickap, E., Çakir, O., 2008. Investigation of mechanical and machinability properties of SiC particle reinforced Al-MMC. *Journal of Materials Processing Technology* 198 (2), 220–225.
- Poddar, P., Mukherjee, S., Saho, K.L., 2009. The microstructure and mechanical properties of SiC reinforced magnesium based composites by rheocasting process. *Journal of Materials Engineering and Performance* 18 (7), 849–855.
- Samal, P., Vundavilli, P.A., Meher, A., Mahapatra, M.M., 2020. Recent progress in aluminium metal matrix composites: a review on processing, mechanical and wear properties. *Journal of Manufacturing Processes* 59, 131–152.
- Rahimi, B., Khosravi, H., Haddad-Sabzevar, M., 2015. Microstructural characteristics and mechanical properties of Al-2024 alloy processed via a rheocasting route. *International Journal of Minerals Metallurgy and Materials* 22, 59–67.
- Sastry, S., Krishna, M., Uchil, J., 2001. A study on damping behaviour of aluminite particulate reinforced ZA-27 alloy metal matrix composites. *Journal of Alloys and Compounds* 314, 268.
- Si, C., Tang, X., Zhang, X., Wang, J., Wu, W., 2017. Microstructure and mechanical properties of particle reinforced metal matrix composites prepared by gas-solid two-phase atomization and deposition technology. *Materials Letters* 201, 78–81.
- Sri Ram Murthy, P., Seetha Rama Rao, Y., 2019. Evaluation of mechanical properties of aluminium alloy-alumina-boron carbide metal matrix composites. *World Journal of Mechanical Engineering* 4 (1), 027–034.
- Srivatsan, T.S., Lavernia, E.J., 1992. Use of spray techniques to synthesize particulate-reinforced metal-matrix composites. *Journal of Materials Science* 27, 5965–5981.
- Tjong, S.C., Ma, Z.Y., 2000. Microstructural and mechanical characteristics of in situ metal matrix composites. *Materials Science and Engineering R Reports* 29 (3), 49–113.
- Verma, R., Sharma, S., Kumar, D., 2017. Analysis of mechanical properties of aluminium based metal matrix composites reinforced with alumina and sic. *International Journal of Engineering Research and Technology* 6 (03), 454–459.
- White, J., Willis, T.C., Hughes, I.R., Palmer, I.G., Jordan, R.M., 1988. In: Kim, Y.W. (Ed.), *Dispersion Strengthened Aluminium Alloys*. Warrendale, PA: Metallurgical Society of AIME.
- Yang, H., She, X.-W., Tang, B.-B., Li, C.-M., Jiang, X.-Q., 2019. Study of the microstructure and ring element segregation zone of spray deposited SiCp/7055Al. *Materials* 12, 1299.
- Ye, H.Z., Liu, X.Y., 2004. Review of recent studies in magnesium. *Journal of Materials Science* 9, 6153–6171.
- Zhang, J., Perez, R.J., Lavernia, E.J., 1993. Documentation of damping capacity of metallic, ceramic and metal-matrix composite-materials. *Journal of Materials Science* 28, 2395–2404.

Futher Reading

Yang, S., 2005. The Behaviour of Compression Deformation and Forging Technology of Spray Deposited 7075/SiCp Composite. (Master of Science thesis). Changsha: Hunan University.

Additive Manufacturing of Metal Matrix Composites

Sankaranarayanan Seetharaman and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composites comprise of a continuous metallic matrix dispersed with hard and strong reinforcement phases typically in the forms of fibers or particles. They exhibit excellent combination of properties like improved strength, elastic modulus and damping characteristics, superior wear resistance, and reduced thermal expansion which are highly suitable for automotive, aerospace, space, defense, sports, electronics and tooling applications.

While MMCs made of Al, Ti, and Mg alloys are commonly recommended for structural lightweighting, Ni based MMCs find applications as high temperature materials. Similarly, Fe and Cu based MMCs are widely used in tooling and electronic packaging industries, respectively. In case of reinforcements, study of available literature highlights the extensive use of Al_2O_3 , SiC, TiC, B_4C in the form of discontinuous particle reinforcements. However, fibers and whiskers made of graphite, SiC and Al_2O_3 are also used for demanding engineering applications (Kainer, 2006).

Traditionally, MMCs are produced using stir casting, melt infiltration, deposition, powder metallurgy and mechanical alloying methods which can be grouped under liquid and solid-state processing methods as shown in Fig. 1.

Each of the above-mentioned conventional methods has their own set of benefits and limitations and the same has been extensively reported in open literature. Recently, MMCs based on Al, Ti, Fe and Ni alloys with superior mechanical properties are also produced using additive manufacturing methods. Additive manufacturing (AM) refer to layer by layer joining of powder to make end-usable products. The benefits of AM over traditional manufacturing include: (1) complex part manufacturing without excess tooling needs, (2) reduced number of processing steps and (3) minimal requirement for post-processing (Gibson *et al.*, 2010b).

The commercial AM processes are broadly classified into three main groups: (1) liquid-based systems, (2) solid-based systems and (3) powder-based systems (Gibson *et al.*, 2010a). While the liquid-based systems are effective for polymer processing, powder and solid-based systems can be utilized for fabricating metallic materials. While all these methods involve a layer-based manufacturing approach starting from the CAD model generation to post-processing/finishing of built parts, they essentially differ by means of: (1) materials that can be used and their initial properties, (2) how the layers are created, and (3) how the layers are bonded to each other. Such differences will eventually determine the accuracy of build part, its properties and performance.

Solid-Based Systems

Material extrusion, ultrasonic consolidation (UC) and electron beam additive manufacturing (EBAM) processes use solid raw material to produce three-dimensional solid objects (Domack and Baughman, 2005; Antonysamy, 2012). While the FDM process commercialized by Stratasys is very popular for making polymer 3D parts through the extrusion of thermoplastic material from a nozzle, metal extrusion is relatively new in which the filament for extrusion is a combination of thermoplastic material and metallic particles (3DEO, 2018). In metal extrusion, the printed parts are compulsorily subjected to post-processing heat treatment process in order to burn out the plastic remains and for better consolidation.

UC patented by Solidica and Sciaky's EBAM techniques can be employed for metallic parts fabrication (Domack and Baughman, 2005; Antonysamy, 2012). UC process produce complex part geometries by sequentially laminating the metal foil layers using an ultrasonic sonotrode to induce vibrations for joining/welding. Unlike other additive technologies wherein the bonding between layers is generated by selective heating/melting of powder materials, UC applies ultrasonic joining technique to produce true metallurgical bonds between layers of metallic materials. This method can be successfully used to manufacture low melting point metal parts with following advantages: (1) higher fabrication speed, (2) no requirement of control atmosphere, and (3) reduced residual stresses and part distortion.

EBAM uses wire feed raw material for fabricating metallic materials. This method promises high deposition rates and ability to fabricate large part sizes. A similar electron beam based free-form fabrication (EBF3) method has been used by NASA to build parts in zero gravity environments.

Powder Based Systems

Nowadays, powder-based AM systems based on laser and electron beam source attract extensive interest in metallic part fabrication. Fig. 2 shows the family tree and basic working principle of different powder bed AM systems.

Binder Jetting involves layer by layer spreading of powder materials which were subsequently joined by selectively applying glue using an inkjet head. The major advantage of this method is that it can be applied for joining metal powders. The major limitation of this process is that it always requires post processing steps such as oven sintering, isostatic pressing etc., as the final product fabricated using this process is not very strong.

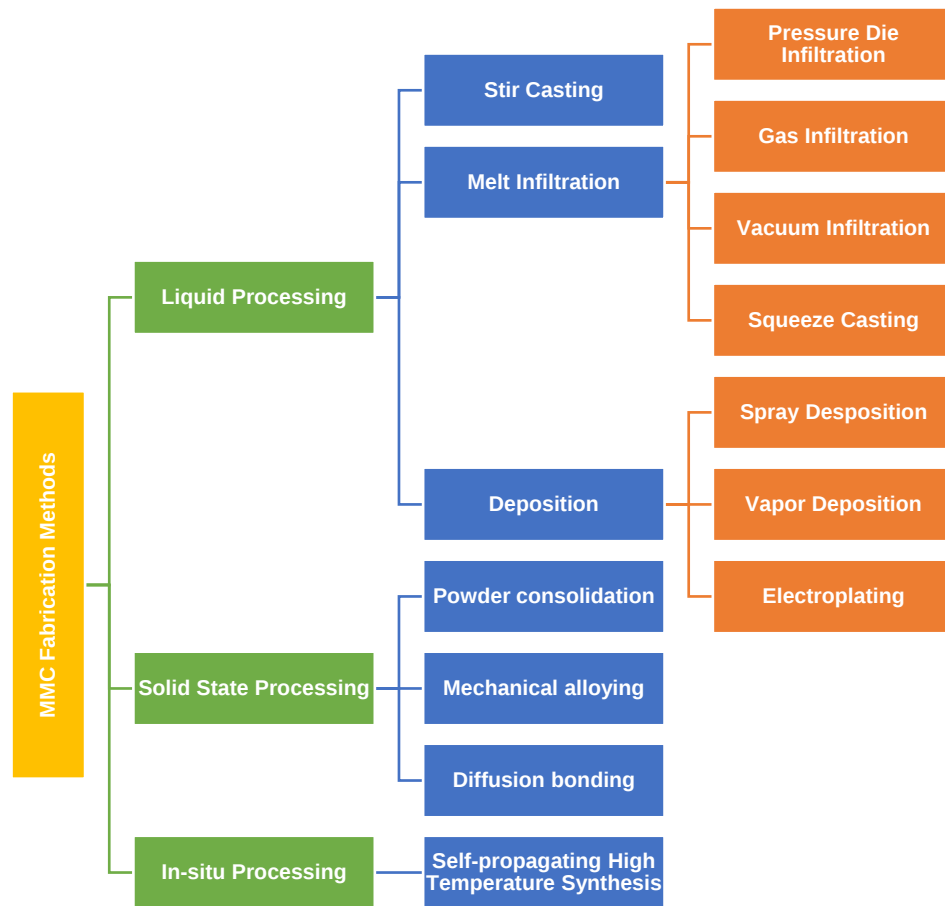


Fig. 1 MMC composite fabrication methods.

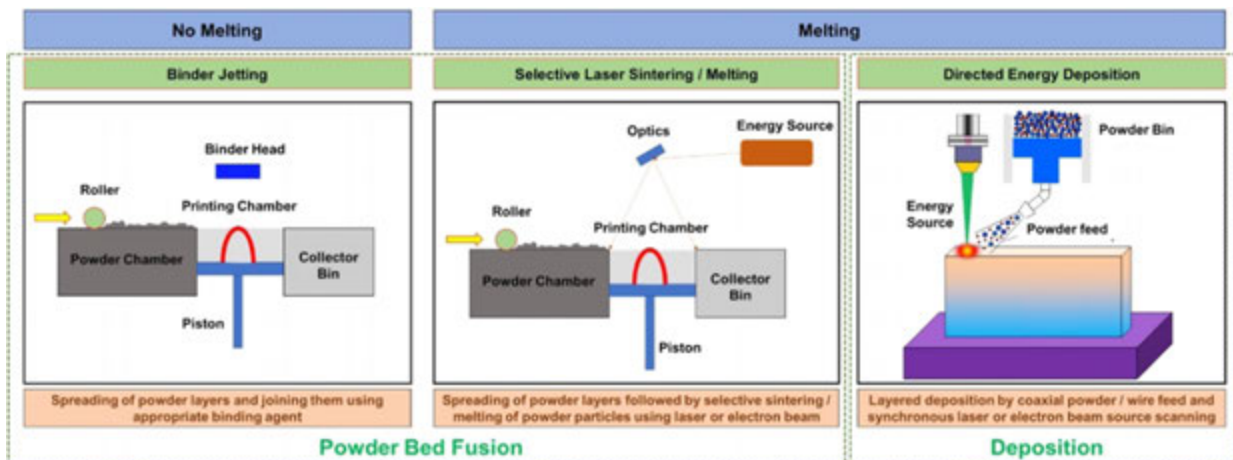


Fig. 2 Powder Bed AM methods. Reproduced from Gibson, I. Rosen, D.W., Stucker, B., 2010b. Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing. Springer. pp.17–40. Li, W., *et al.*, 2017a. Effect of optimizing particle size on directed energy deposition of functionally graded material with blown pre-mixed multi-powder. Manufacturing Letters 13. Available at: <https://doi.org/10.1016/j.mfglet.2017.07.001>. Zhang, J., *et al.*, 2019. A review of selective laser melting of aluminum alloys: Processing, microstructure, property and developing trends. Journal of Materials Science and Technology 35. Available at: <https://doi.org/10.1016/j.jmst.2018.09.004>. Ziaee, M., Crane, N.B., 2019. Binder jetting: A review of process, materials, and methods. Additive Manufacturing 28. Available at: <https://doi.org/10.1016/j.addma.2019.05.031>.

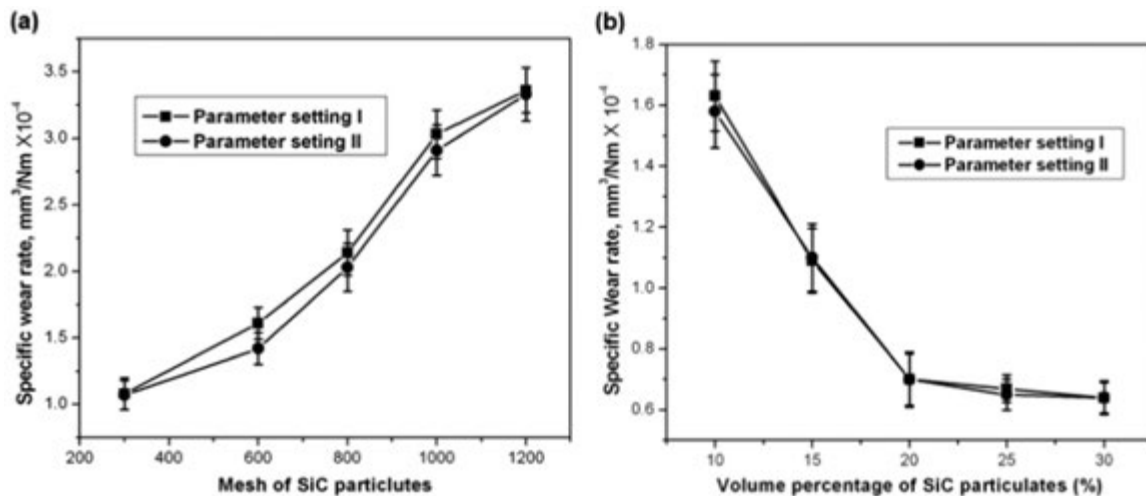


Fig. 3 Wear resistance of SiC/Al MMCs reported by (Ghosh and Saha). Reproduced from Ghosh, S.K., Saha, P., 2011. Crack and wear behavior of SiC particulate reinforced aluminium based metal matrix composite fabricated by direct metal laser sintering process. *Materials and Design* 32. Available at: <https://doi.org/10.1016/j.matdes.2010.06.020>.

Laser sintering (LS) process was first developed at the University of Texas. This process involves layer by layer spreading of powder and subsequent sintering using a low power (CO₂) laser source. The general processing procedure includes a roller to deposit a fine layer of powder on the build platform. The laser source (typically 50 W) will then selectively sinter the powder and completes the fabrication of one layer. For the next layer, the powder bed is then lowered by one-layer thickness and the new layer of powder material is then deposited and sintered. This process is continued until the complete part is produced. As the power of the laser in the SLS machine is not enough to melt metals and ceramics, they are often coated with the polymer which acts as a binder. After sintering, the binder is removed (by burning) and then the mold is infiltrated with a low melting point metal or alloy.

Laser Melting (LM) is very similar to sintering process, except that a high power (fiber) laser source is used to selectively melt the uncoated metal powders melted to produce high-strength metallic parts. This method shows better suitability to produce full dense parts approaching 99.9% density in a direct way, without post-infiltration, sintering or hot isostatic pressing. Since the selective laser melting (SLM) process does not require burning out of polymer and post-densification, the time required for producing a metal part is reduced in SLM when compared to the SLS process. Another major advantage lies in its high feasibility in processing non-ferrous metals such as Ti, Al, Cu, which cannot be well processed using partial melting and associated high viscosity and balling phenomenon. However, the high energy level required for melting the powder materials and the risk of unstable melt pool resulting in large shrinkage and residual stress are regarded as key limitations. Currently, the LM machines are marketed by 3D systems, Concept laser, EOS, SLM, AddUp, Trumpf and Matsuura.

Electron Beam Melting (EBM) process developed at Chalmers University of Technology, Sweden and marketed by Arcam, works on the similar principle as selective laser melting except that the melting of powder materials was done using a focused electron beam emitted from a heated tungsten filament. The electron beam interacts with the metal powder on the platform so that the kinetic energy of the electron beam is converted to heat and melts the region of the metal powder. Since this process requires high vacuum for electron beam processing, better mechanical properties can be achieved by using EBM process. However, the EBM process has few limitations such as: (1) process stability, (2) part defects, (3) quality variations, and (4) size of building chamber.

Laser Deposition (LD) methods involve localized melting and deposition of powder materials using a high-power laser source. The carrier medium which is usually an inert gas feeds the powder through nozzles. Upon interaction with laser, the powder melts and the molten material is deposited on the platform based on the CAD data. This technology has been commercialized by POM, Optomec, Aeromet and MTS as direct metal deposition (DMD), laser engineered net shaping (LENS), laser rapid forming (DRF), laser cladding (LC), and laser additive manufacturing (LAM) respectively. The deposition methods can be effectively used to produce titanium alloys, nickel alloys, steels, cobalt alloys, aluminum alloys and composite coatings. Their advantages include: (1) production of fully dense materials with good metallurgical properties at reasonable speeds, (2) capability to build intricate features and shapes, (3) ability to integrate features to cast or forged parts for repair purposes. The major limitations are: (1) difficulty in building overhung parts and features, (2) microstructural control, (3) poor surface finish, and (iv) residual stress.

Although there have been only a limited number of commercial materials that can be used in AM processes, the aerospace, automotive and tooling industries are successful in adopting the additively manufactured metallic materials for applications in automobile brackets, gas turbines, heat exchangers, reactor vessels, conformal cooling etc. While the additive manufactured MMCs exhibit excellent properties that are comparable/superior to that of other conventional manufacturing methods, issues related to processing and properties such as residual porosity, cracks, mechanical anisotropy, residual stress and poor surface finish resulting from additive processing need better understanding on process-structure-property relationships. In this article, an attempt has been

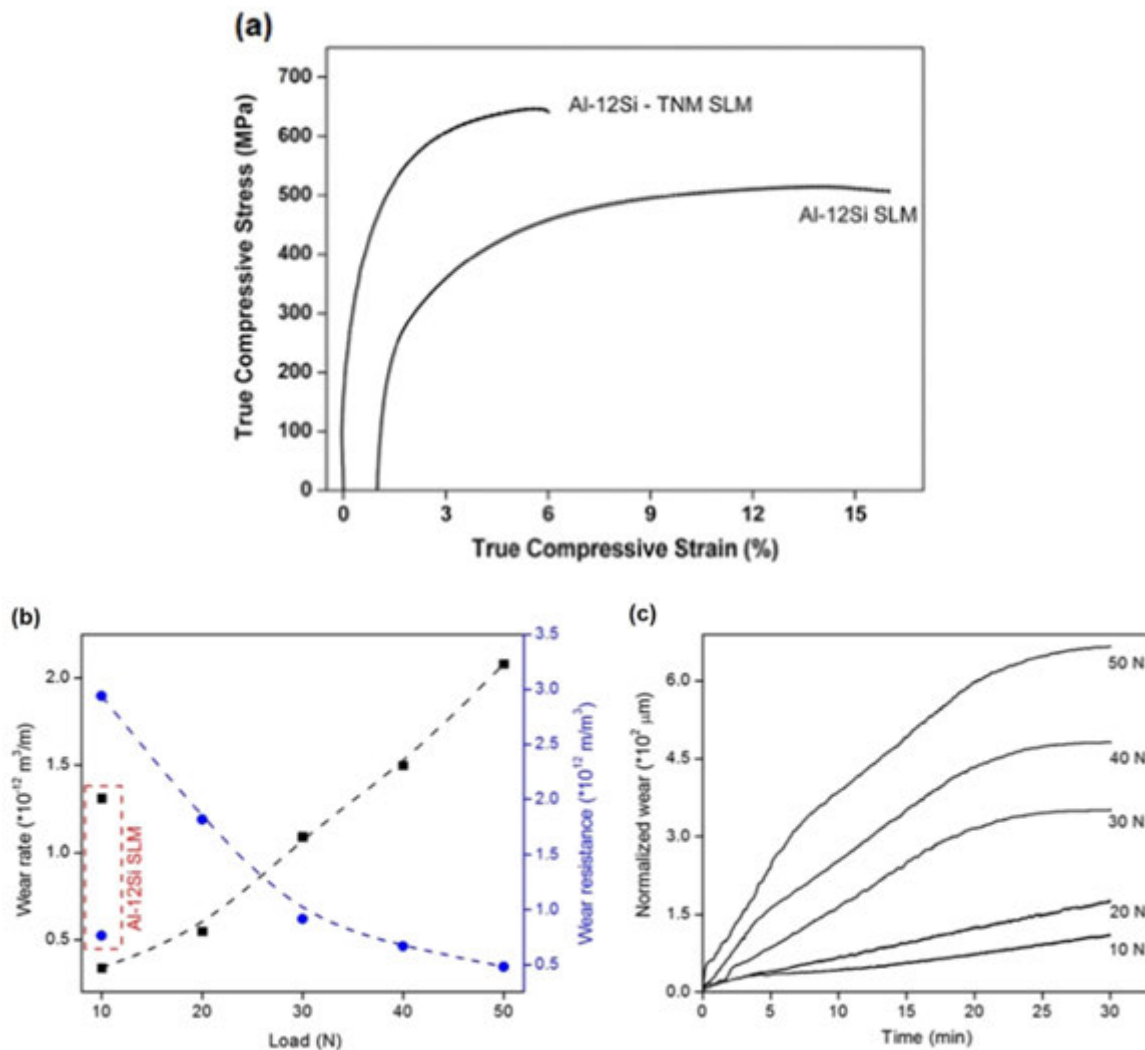


Fig. 4 Compressive response and wear resistance of SLM processed Al-12Si-TNM composites reported by (Prashanth *et al.*). Reproduced from Prashanth, K.G., *et al.*, 2016. Processing of Al-12Si-TNM composites by selective laser melting and evaluation of compressive and wear properties. Journal of Materials Research 31. Available at: <https://doi.org/10.1557/jmr.2015.326>.

made to summarize the research progress made so far on the laser additive manufacturing of metal matrix composites based on aluminum, titanium, nickel, iron and copper alloys.

Additive Manufacturing of Aluminum Matrix Composites

Aluminum matrix composites (AMC) are widely recommended for the structural light weighting of automobiles. The additive manufacturing of AMC was first performed by Ghosh *et al.* (2010); Ghosh and Saha (2011) using a self-assembled primitive set up containing NDYAG laser source. In this work, the effects of particle size and volume fraction of SiC particle reinforcement were assessed in terms of the density, microstructure, hardness and wear resistance of the developed composites. While the use of 300 mesh size SiC particles imparted better density, improved hardness was achieved in the case of 1200 mesh size SiC reinforcement. The cracking susceptibility was found to increase significantly when the SiC content extended beyond 15 vol% SiC. The results also showed adverse effects on wear resistance with increasing reinforcement size and content beyond 20 vol% Figs. 3–10.

Al-12Si matrix reinforced with TNM (Ti52.4Al42.2Nb4.4Mo0.9B0.06, at%) particles were produced using selective laser melting by Prashanth *et al.* (2016). The reaction between TNM particles and the matrix produced Al_6MoTi intermetallic phases to improve the compressive strength and wear resistance of the composite Figs. 11–17.

In a similar study, 40 vol% TiB_2 reinforced Al-12Si coatings were prepared using the method of laser cladding (Anandkumar *et al.*, 2011). As expected, the developed AMC coatings exhibited better hardness ($156 \text{ HV}_{0.1}$) and superior wear resistance ($2.65 \times 10^{-5} \text{ mm}^3/\text{Nm}$) compared to monolithic alloy due to the microstructural composition containing primary α -Al-dendrites +

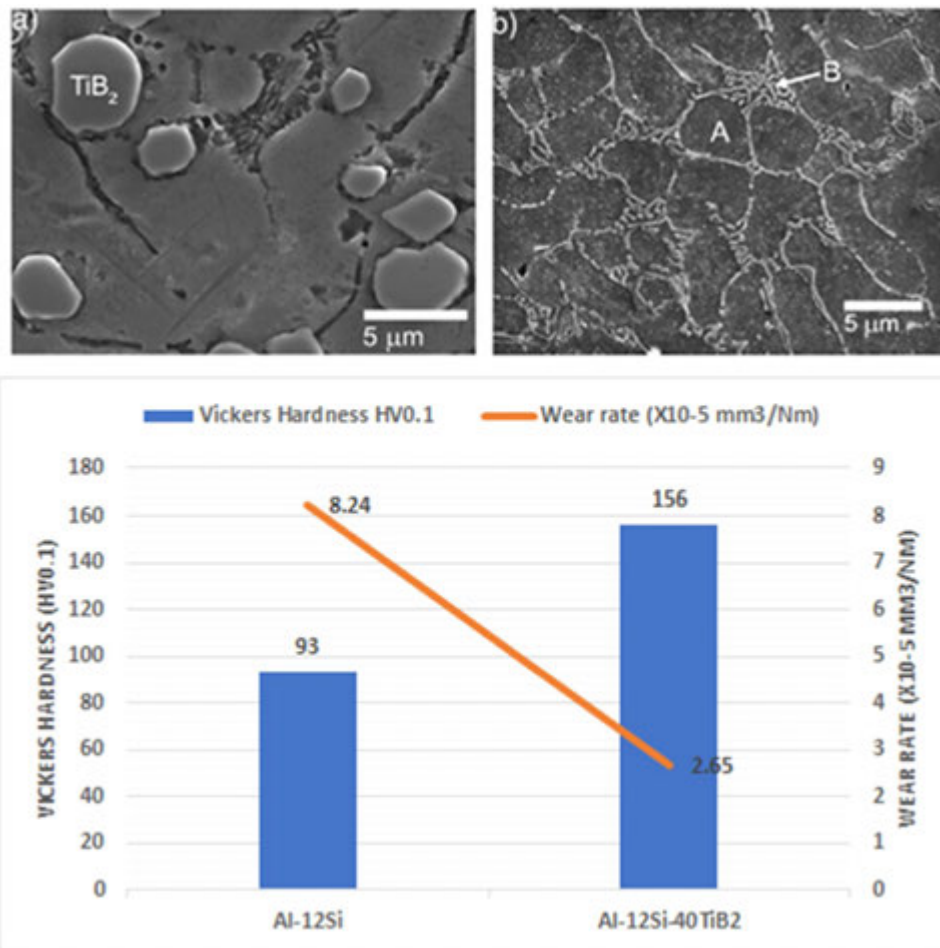


Fig. 5 Microstructure and mechanical properties of Al-12Si-40TiB₂ composite from (Anandkumar *et al.*). Reproduced from Anandkumar, R., Almeida, A., Vilar, R., 2011. Wear behavior of Al-12Si/TiB₂ coatings produced by laser cladding. Surface and Coatings Technology 205. Available at: <https://doi.org/10.1016/j.surfcoat.2011.01.048>.

inter-dendritic Al-Si eutectics and the uniformly distributed TiB₂ particles. Additionally, the results reported no reaction products contributing towards a clear interfacial load transfer to achieve a hardness of 156 Hv and lower wear rate **Figs. 18–23**.

Lorusso *et al.* (2016) also reported the improvement in wear resistance due to TiB₂ reinforcements. In this study, AlSi10Mg alloy and its composites reinforced with micro (10 wt%) and nano (1 vol%) sized TiB₂ particles were produced by direct metal laser sintering (DMLS) technique. The end properties of DMLS processed materials were also compared to that of the cast AlSi10Mg alloy **Tables 1–5**.

In a similar study, Chang *et al.* (2015) performed the selective laser melting of SiC/AlSi10Mg composite powder with different SiC particle size. Here the in-situ chemical reaction between SiC and AlSi10Mg resulted in hybrid (Al₄SiC + SiC) phases and the extent of in-situ reaction was found to enhance with increasing SiC content. The results showed at least 50% increase in micro-hardness and ~66% reduced wear rate for the composites.

Similar observations were also reported by Gu *et al.* (2015) and Zhao *et al.* (2019) where multiple phases like un-melted SiC, Al₄SiC₄, and eutectic SiC developed due to the in-situ chemical reaction. Similarly, the selective laser melting of Al₂O₃/AlSi10Mg composites powder produced in-situ produced Al₂Si₄O₁₀ phases reinforced AMCs (Jue and Gu, 2017). In case of Fe₂O₃ reinforcements, the in-situ chemical reaction produced α-Al₂O₃, Al-Fe intermetallics together with crystalline Si depending on the base matrix chemical composition (Dadbakhsh and Hao, 2014).

Aversa *et al.* (2017) prepared a composite blend of AlSi10Mg matrix containing micro or nanoscale TiB₂/MgAl₂O₄ reinforcements and used them to fabricate the respective bulk metallic composites using the method of DMLS. In this study, mechanical characterization results revealed lower yield and tensile strengths for all the composite formulations when compared to AlSi10Mg base alloy which was attributed to the relatively coarser microstructure of the composites developed due to the difference in volumetric energy density requirements.

A similar study reported the composite formation mechanism in SLM processed nano-TiC reinforced AlSi10Mg composite (Gu *et al.*, 2009). In this study, a higher densification was achieved only by optimizing the laser energy input per unit length at 700 J/m

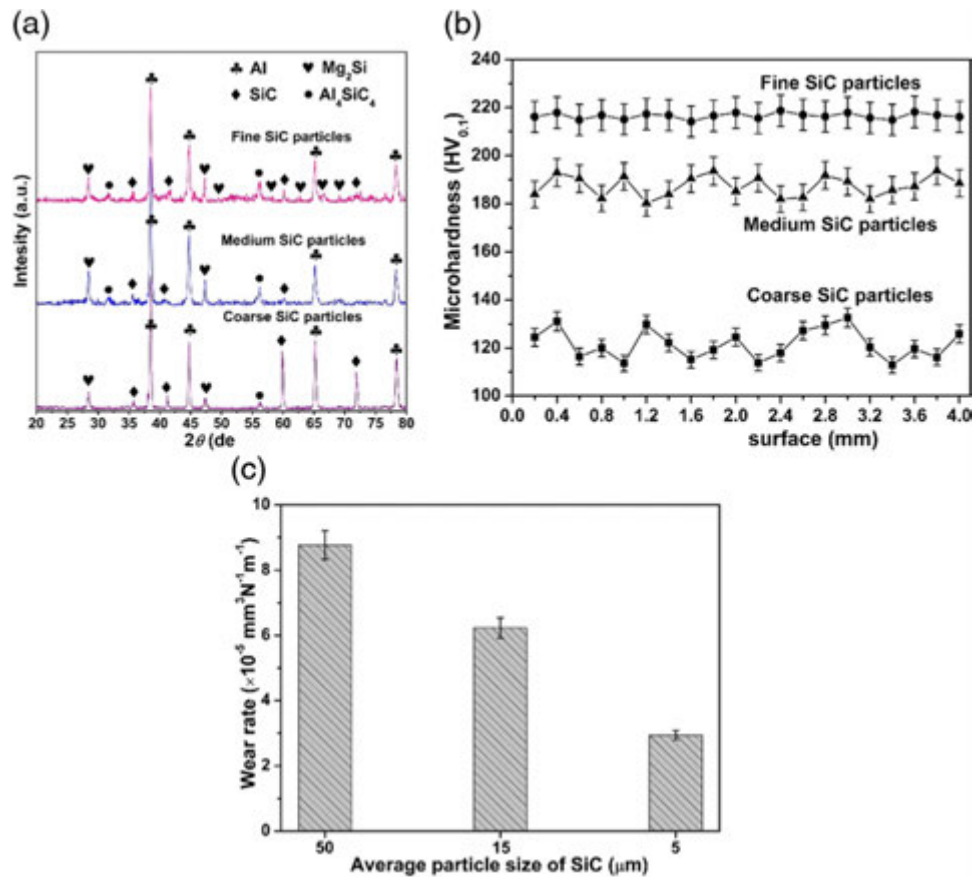


Fig. 6 Properties of SLM processed hybrid ($Al_4SiC_4 + SiC$) reinforced Al Composites Modified from Chang, F., *et al.*, 2015. Selective laser melting of in-situ $Al_4SiC_4 + SiC$ hybrid reinforced Al matrix composites: Influence of starting SiC particle size. *Surface and Coatings Technology* 272, 15–24. Available at: <https://doi.org/10.1016/j.surfcoat.2015.04.029>.

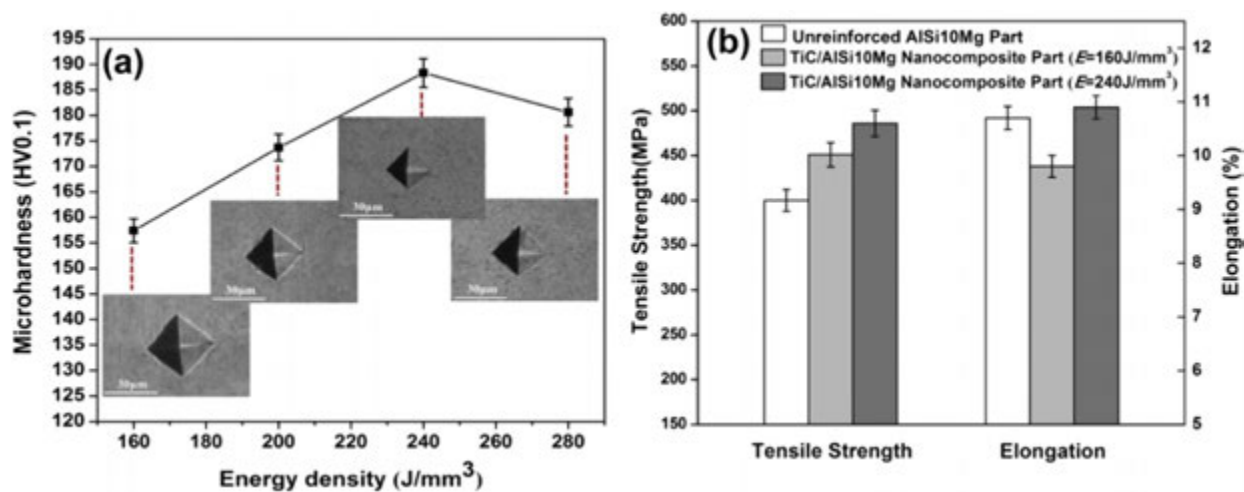


Fig. 7 Mechanical properties of TiC/AlSi10Mg nanocomposites from Gu *et al.* Reproduced from Gu, D., *et al.*, 2015. Rapid fabrication of Al-based bulk-form nanocomposites with novel reinforcement and enhanced performance by selective laser melting. *Scripta Materialia* 96. Available at: <https://doi.org/10.1016/j.scriptamat.2014.10.011>.

and the insufficient energy inputs resulted in significant balling and porosity. This is because when the energy input is high, the larger melt pool and associated marangoni flow interacts with the solid particles to cause agglomeration/clustering. On the other hand, the lower intensity of thermocapillary flow and the shorted melt pool life prevents particle agglomeration at low energy

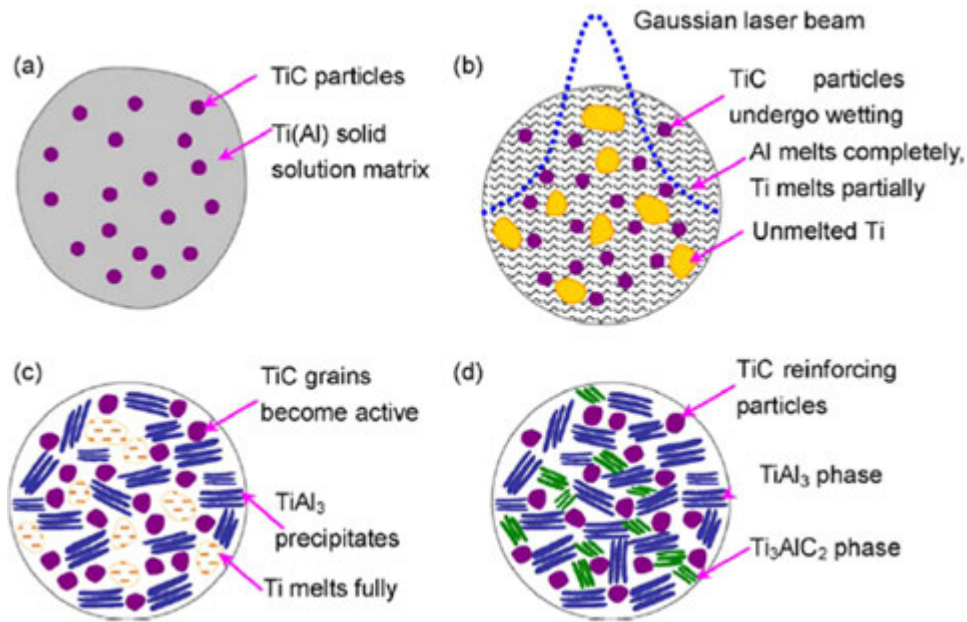
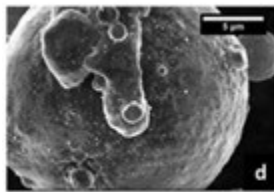


Fig. 8 Composite formation mechanism during SLM processing. Reproduced from Gu, D., *et al.*, 2009. In-situ TiC particle reinforced Ti-Al matrix composites: Powder preparation by mechanical alloying and selective laser melting behavior. *Applied Surface Science* 255. Available at: <https://doi.org/10.1016/j.apsusc.2009.07.008>.



Composition	Vol. Density (J/mm ³)	Energy (J/mm ³)	Young's Modulus (GPa)	Yield Strength (MPa)	Ultimate Strength (MPa)	Elongation at break (%)
AlSi10Mg*	47.8		73±3	257±2	384±2	6.7±0.8
AlSi10Mg*	81.3		71±2	203±3	301±6	5.4±0.4
AlSi10Mg/MgAl ₂ O ₄ nanocomposite*	81.3		76±1	198±1	323±3	6.3±0.7

* Stress relieved at 300° for 2 h

Fig. 9 Powder microstructure and the mechanical properties of MgAl₂O₄ reinforced AlSi10Mg composite. Reproduced from Marchese, G., *et al.*, 2018. Development and characterisation of aluminium matrix nanocomposites AlSi10Mg/MgAl₂O₄ by laser powder bed fusion. *Metals* 8. Available at: <https://doi.org/10.3390/met8030175>.

input. Hence, the dispersion of nano-scale reinforcement and composite densification strongly depends on the laser processing parameters.

In another recent study, Marchese *et al.* (2018) prepared a composite mixture of AlSi10Mg and nano-MgAl₂O₄ particles by dry mixing and ball-milling. The composite mixture was then processed using laser powder bed fusion technique with a combination of process parameters. While the end mechanical properties of the base alloy and the nanocomposite were largely influenced by the volumetric energy density inputs, the nanocomposite exhibited inferior properties post heat treatment.

Similar observations were also reported by Famodimu (2016) for SLM processed AlSi10Mg/SiC prepared using the ball-milled composite precursor. However, the properties were reported to be comparable to that of conventionally processed composites.

In a recent study, Li *et al.* (2017b) used a gas atomized composite precursor of nano-TiB₂ dispersed AlSi10Mg alloy for selective laser melting. The microstructure of composite developed in this study was significantly different when compared to those composites prepared by the laser melting of simply mixed or mechanical alloyed powder mixture. The use of gas atomized powder contributed towards better interface tailoring compared to particle agglomerates which are common otherwise. Also, a better strength was realized due to a finer microstructure with random crystallographic texture. This study highlighted the use of composite powder precursor for selective laser melting to produce dense and defect free AMCs with superior mechanical properties although the preprocessing is expensive when compared to mechanical alloying.

Recently several attempts have also been made to develop carbon nanotubes (CNT) reinforced AMCs using the method of selective laser melting (Zhao *et al.*, 2016; Wang *et al.*, 2017). While a finer microstructure and better strength of the composite were realized due to laser processing, the direct interaction with the laser source was found to decompose the CNTs.

Using the method of friction deposition, (Karthik *et al.*, 2017) fabricated a metal-metal composite consisting of AA5083 alloy matrix containing 12 vol% nanocrystalline CoCrFeNi high-entropy alloy reinforcement particles. In this study, the inert nature of high entropy alloy reinforcement contributed towards a clear layer-to-layer and reinforcement/matrix interfaces. Also, the

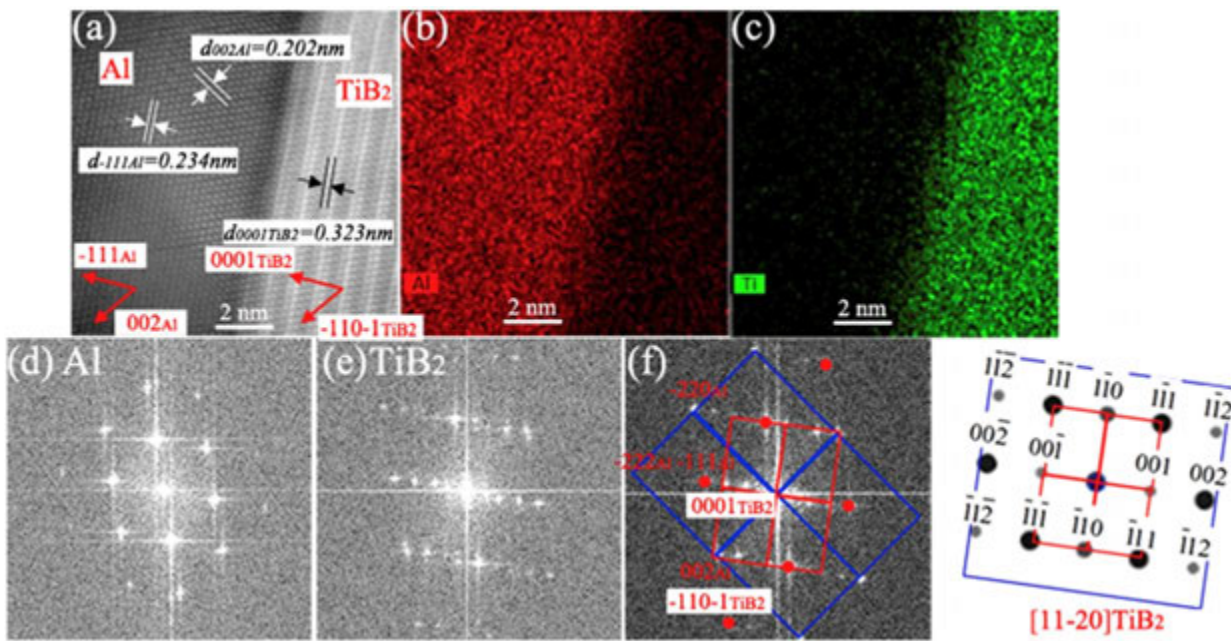


Fig. 10 Microstructural characteristics of nano-TiB₂ dispersed AlSi10Mg composite fabricated by (Li *et al.*). Reproduced from Li, X.P., *et al.*, 2017b. Selective laser melting of nano-TiB₂decorated AlSi10Mg alloy with high fracture strength and ductility. *Acta Materialia* 129. Available at: <https://doi.org/10.1016/j.actamat.2017.02.062>.

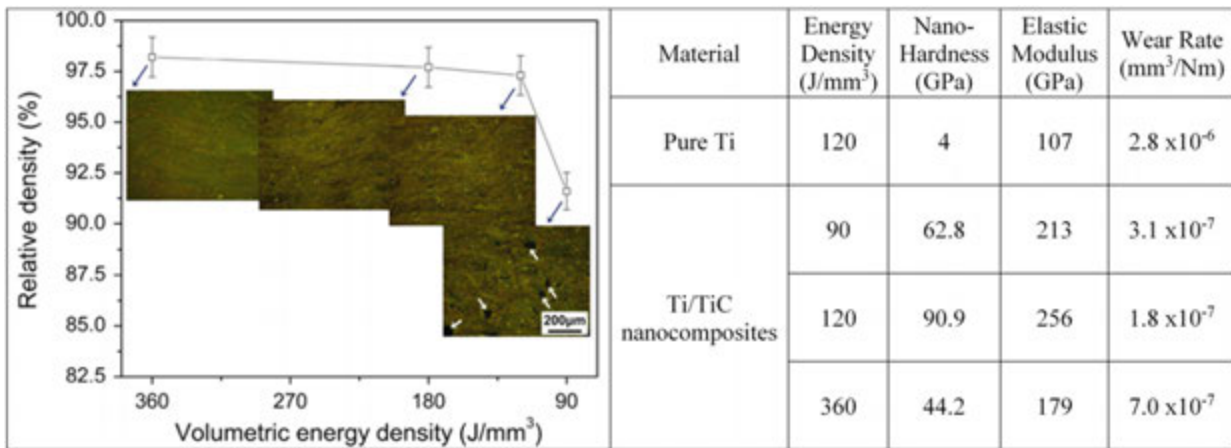


Fig. 11 SLM processing of TiC/Ti composites by (Gu *et al.*). Reproduced from Gu, D., *et al.*, 2011. Nanocrystalline TiC reinforced Ti matrix bulk-form nanocomposites by selective laser melting (SLM): Densification, growth mechanism and wear behavior. *Composites Science and Technology* 71. Available at: <https://doi.org/10.1016/j.compscitech.2011.07.010>.

composite showed better tensile and compressive strengths and ductility than the conventionally processed wrought alloy and composite counterparts.

Additive Manufacturing of Titanium Matrix Composites (TMCs)

Recently there has been a focused attention on the additive manufacturing of TMCs for applications in aircraft engines and structures. However, the additive processing poses some serious challenges in densification due to significantly different densities, viscosities and melting/solidification behaviors between the matrix and reinforcements, unavailability of composite feedstock, and oxidation issues during powder processing etc. Hence an attempt has been made in this section to summarize the progress on additive manufacturing of titanium matrix composites with respect to the critical aspects such as processing, microstructure, mechanical and tribological properties.

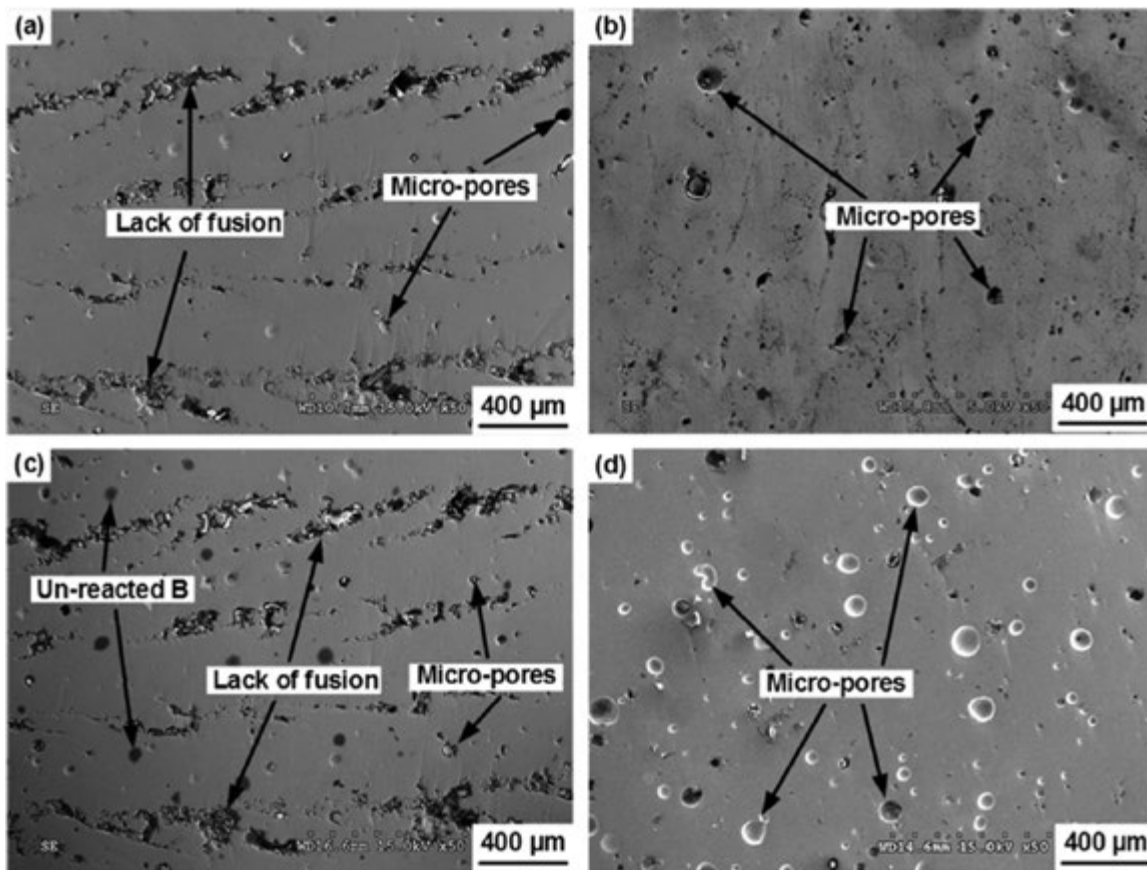


Fig. 12 SEM images of pure Ti processed at (a) 125 W, (b) 200 W, and TiB/TiC composite processed at (c) 125 W; and (d) 200 W. Reproduced from Hu, Y., Ning, F., *et al.*, 2018. Laser engineered net shaping of quasi-continuous network microstructural TiB reinforced titanium matrix bulk composites: Microstructure and wear performance. *Optics and Laser Technology* 99. Available at: <https://doi.org/10.1016/j.optlastec.2017.08.032>.

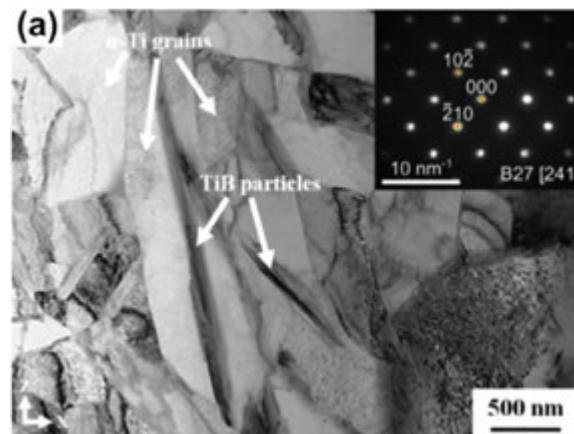


Fig. 13 TEM images showing needle shaped TiB particles in TiB/Ti composite. Reproduced from Attar, H., *et al.*, 2014a. Selective laser melting of in situ titanium-titanium boride composites: Processing, microstructure and mechanical properties. *Acta Materialia* 76. Available at: <https://doi.org/10.1016/j.actamat.2014.05.022>.

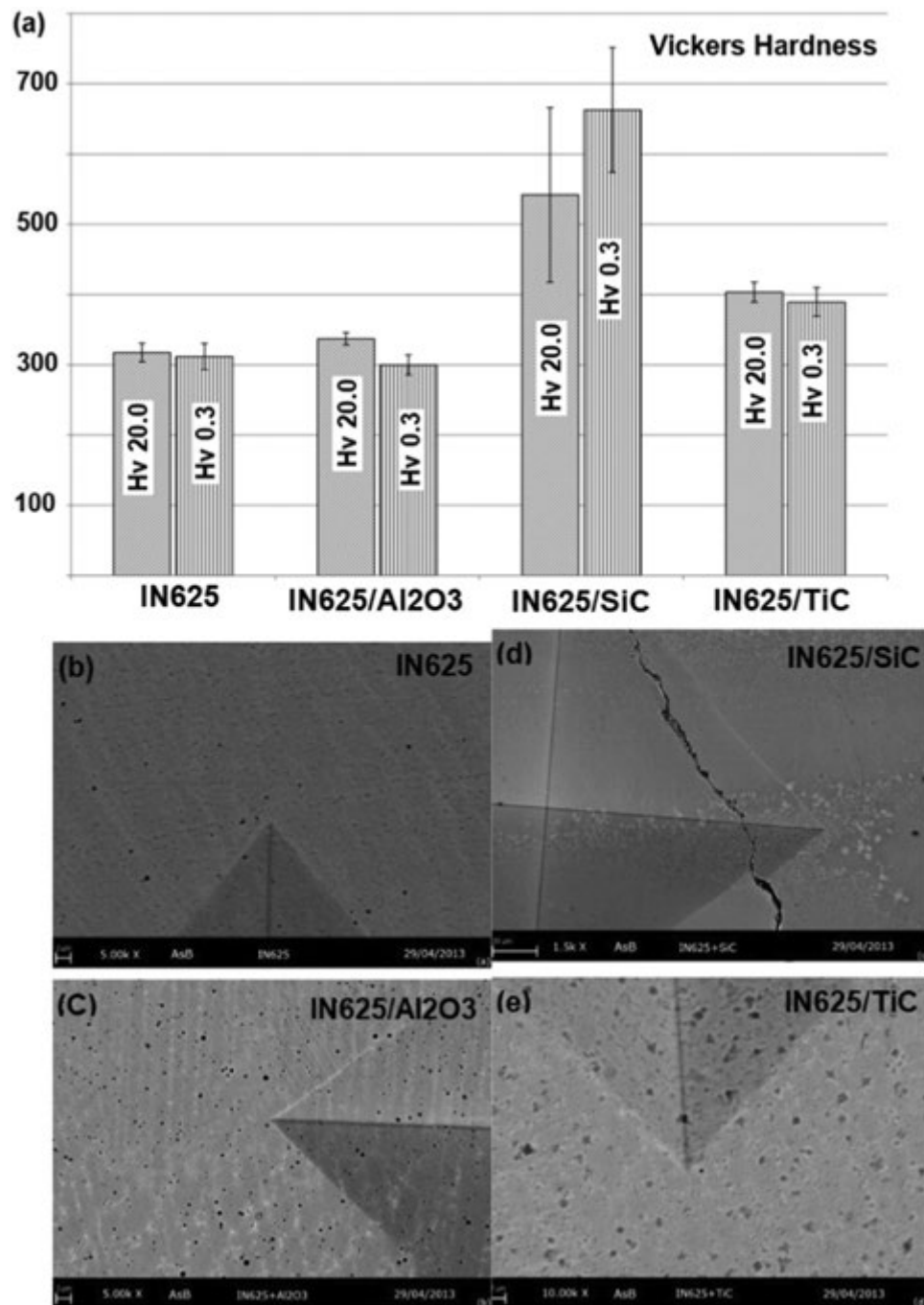


Fig. 14 Results of hardness measurements from (Cooper *et al.*). Reproduced from Cooper, D.E., *et al.*, 2013. Additive layer manufacture of Inconel 625 metal matrix composites, reinforcement material evaluation. Journal of Materials Processing Technology 213. Available at: <https://doi.org/10.1016/j.jmatprotec.2013.06.021>.

Liu and DuPont (2003) employed the LENS process to produce TiC reinforced functionally graded Ti-composites in which the TiC particles content was varied upto 95 vol% without any cracking issues. In a similar study (Zhang *et al.*, 2008), the increasing TiC content has resulted in larger amount of unmelted TiC particles that are uniformly distributed in the alloy matrix to contribute towards marginal improvement in hardness, strength and wear resistance. However, the ductility was adversely affected.

Wang *et al.* (2007) used Ti64 wires and TiC powder to fabricate Ti64/TiC composites. In this study, the TiC content was varied from 8 to 74 vol%. While the mechanical characterization results showed better yield and ultimate strengths for 8 vol% TiC addition, but the ductility was adversely affected. The wear resistance of TMCs improved till 15 vol% TiC addition.

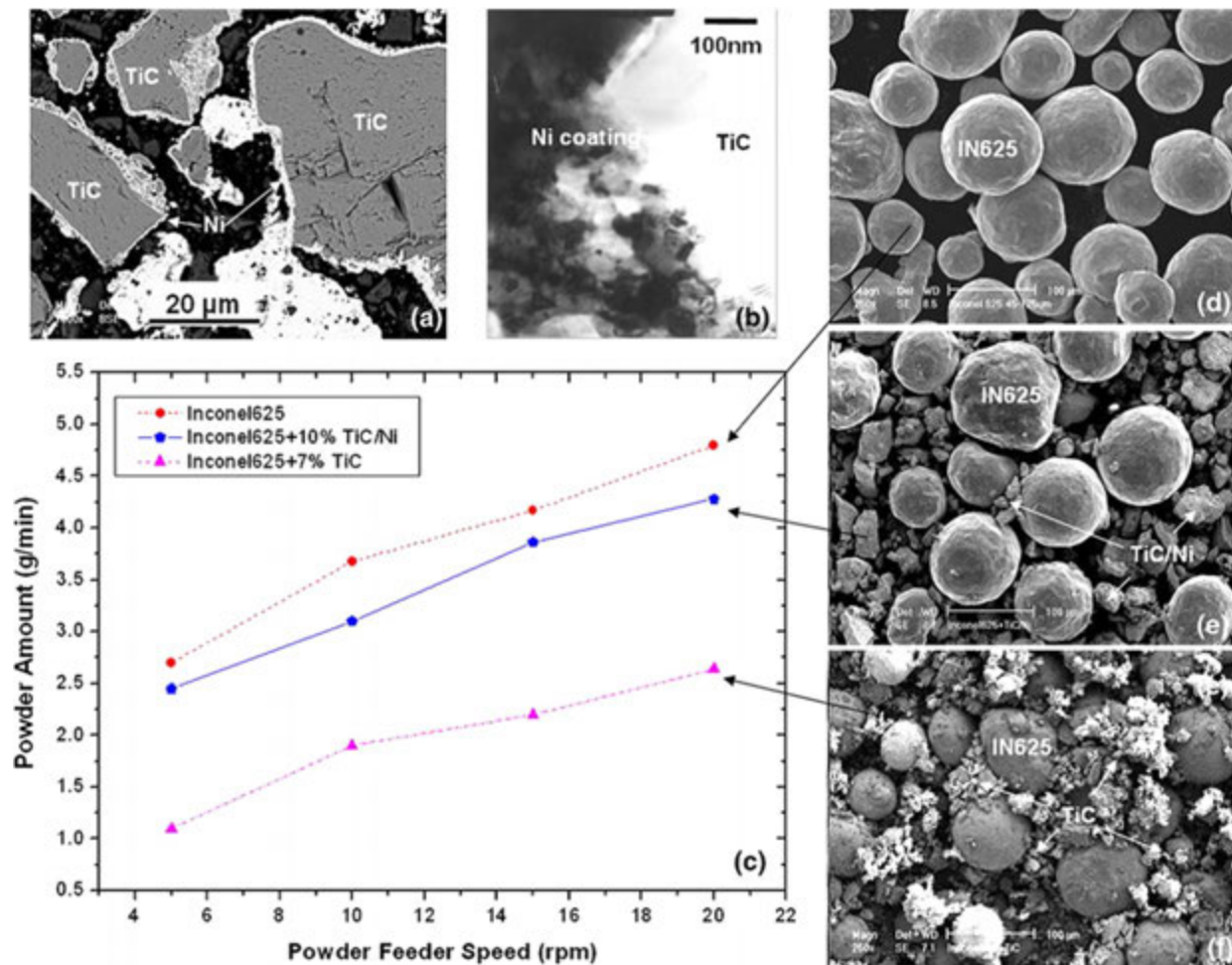


Fig. 15 Results of powder flowability measurements from (Zheng *et al.*). Reproduced from Zheng, B., *et al.*, 2010. The influence of Ni-coated TiC on laser-deposited IN625 metal matrix composites. Metallurgical and Materials Transactions A 41. Available at: <https://doi.org/10.1007/s11661-009-0126-5>.

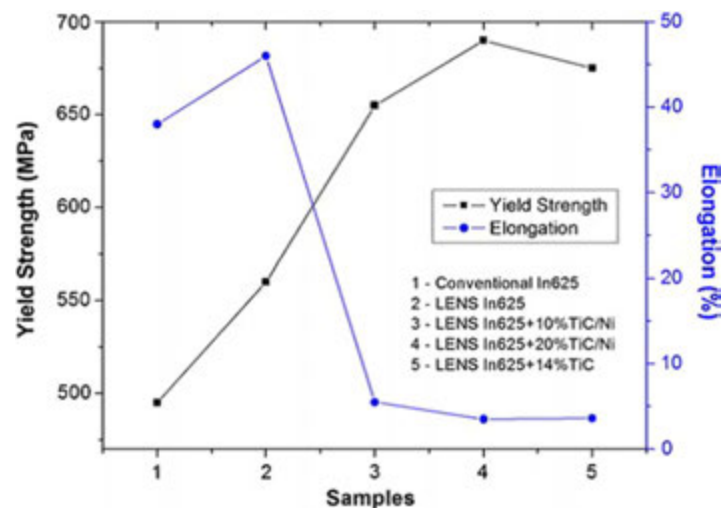


Fig. 16 Tensile test result of LENS-deposited IN625 alloy and composites. From Reproduced from Zheng, B., *et al.*, 2010. The influence of Ni-coated TiC on laser-deposited IN625 metal matrix composites. Metallurgical and Materials Transactions A 41. Available at: <https://doi.org/10.1007/s11661-009-0126-5>.

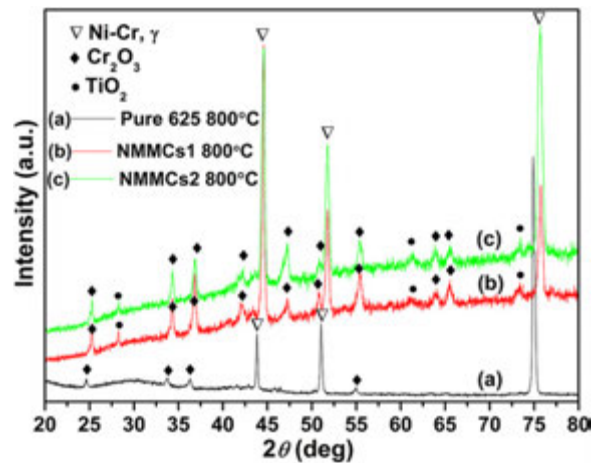


Fig. 17 Combined presence of Cr_2O_3 and TiO_2 in the oxidized layer of TiC/IN625 composite. Reproduced from Hong, C., Gu, D., Dai, D., Cao, S., *et al.*, 2015b. High-temperature oxidation performance and its mechanism of TiC/Inconel 625 composites prepared by laser metal deposition additive manufacturing. *Journal of Laser Applications* 27 (S1), (S17005). Available at: <https://doi.org/10.2351/1.4898647>.

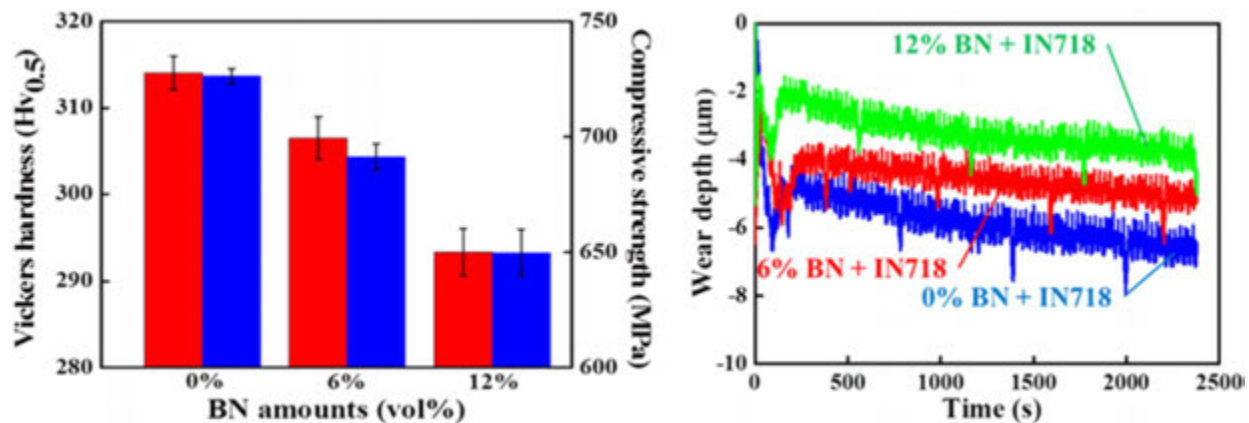


Fig. 18 Vicker hardness and wear response of BN/IN718 composites. Reproduced from Kim, S.H., *et al.*, 2017. Thermo-mechanical improvement of Inconel 718 using ex situ boron nitride-reinforced composites processed by laser powder bed fusion. *Scientific Reports* 7. Available at: <https://doi.org/10.1038/s41598-017-14713-1>.

Gu *et al.* (2011) investigated the properties of Ti/TiC composites processed using selective laser melting of ball-milled Ti-15 wt%TiC composite mixture. In this study, the energy density input was found to significantly affect the microstructural evolution and the mechanical properties of developed composites. While the maximum energy density ($\sim 350 \text{ J/mm}^3$) produced a finer microstructure with uniformly distributed TiC particles, coarser dendrites and reinforcement agglomerates were reported for lower energy density levels. Similarly, better mechanical properties were achieved for energy densities more than 120 J/mm^3 . However, the mechanical properties were found to deteriorate when the energy density was significantly higher than 350 J/mm^3 .

The authors also investigated the influence of TiC content on the properties of Ti/TiC composites (Gu *et al.*, 2012). It was found that the increasing TiC content has a negative impact on the densification behavior as the melting and consolidation of the Ti-matrix along with TiC reinforcement becomes increasingly difficult. While the composite containing less than 15 wt% TiC showed better reinforcement distribution within the fine lamellar structured matrix, clustering was reported beyond 17.5 wt%TiC addition. Similarly, Kun *et al.* (2017) also reported the enhanced tensile strength of Ti/TiC nanocomposites due to the formation and uniform dispersion of nanoscale SiC during the SLM process.

Titanium boride reinforced Ti-MMCs were produced through the LENS processing of the elemental mixture containing Ti and B particles (Banerjee *et al.*, 2005). Microstructural characterization of the deposited composites showed fine microstructure with uniformly distributed TiB particles due to faster cooling rates in as-deposited state, whereas the microstructure was coarsened post heat treatment. Hu and Cong, (2018); Hu and Ning (2018) developed LENS deposited Ti/TiB composites from a blend of ball-milled Ti64 alloy and elemental boron. In this case too, a very fine distribution of needle shaped TiB precipitates with a clean interface and strong mechanical/chemical bonding with α/β Ti-matrix was reported which resulted in improved mechanical properties and wear resistance. In another study (Samuel *et al.*, 2008; Nag *et al.*, 2009), the same research group reported the LENS

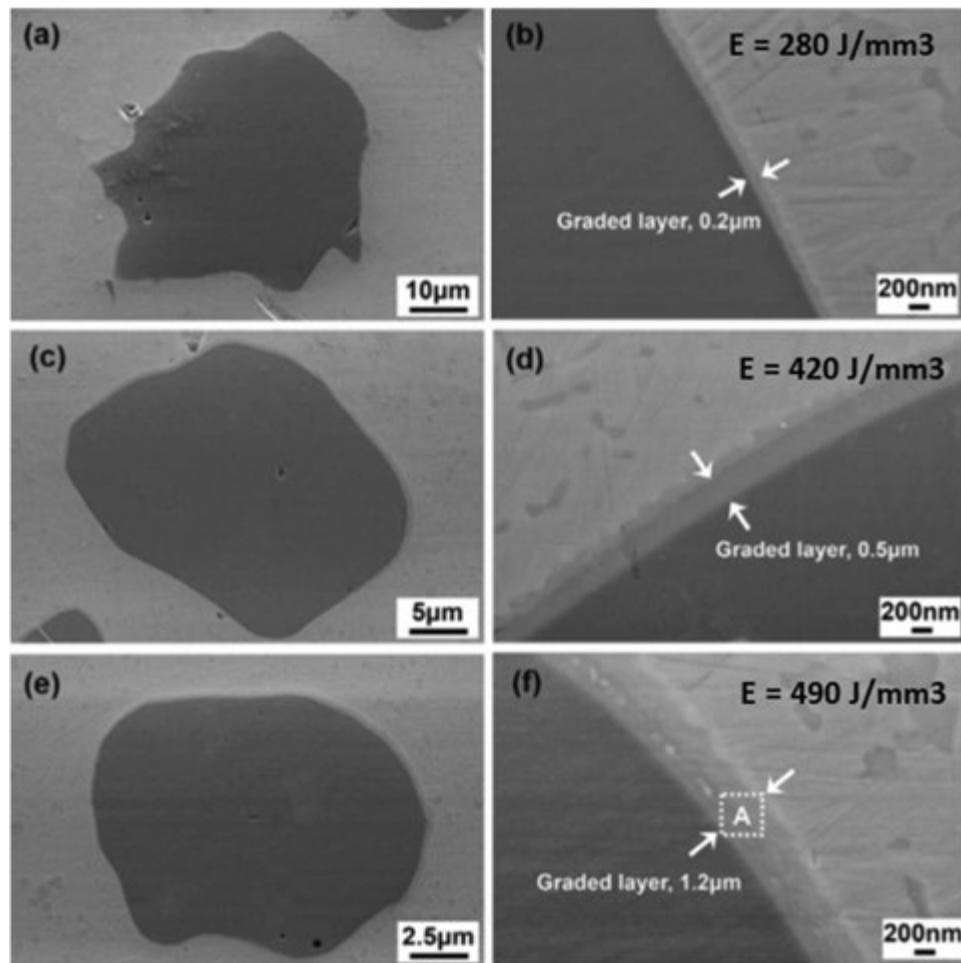


Fig. 19 Interfacial characteristics of TiC/IN718 composite processed at (a-b) 280 J/mm³, (c-d) 420 J/mm³ and (e-f) 490 J/mm³. Reproduced from Gu, D., *et al.*, 2014. Combined strengthening of multi-phase and graded interface in laser additive manufactured TiC/Inconel 718 composites. *Journal of Physics D Applied Physics* 47. Available at: <https://doi.org/10.1088/0022-3727/47/4/045309>.

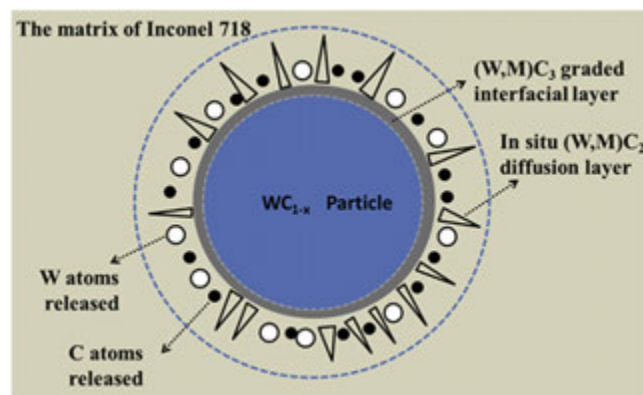


Fig. 20 Schematic showing the formation of graded interfacial layer in WC/IN718. Reproduced from Rong, T., Gu, D., 2016. Formation of novel graded interface and its function on mechanical properties of WC1-x reinforced Inconel 718 composites processed by selective laser melting. *Journal of Alloys and Compounds* 680. Available at: <https://doi.org/10.1016/j.jallcom.2016.04.107>.

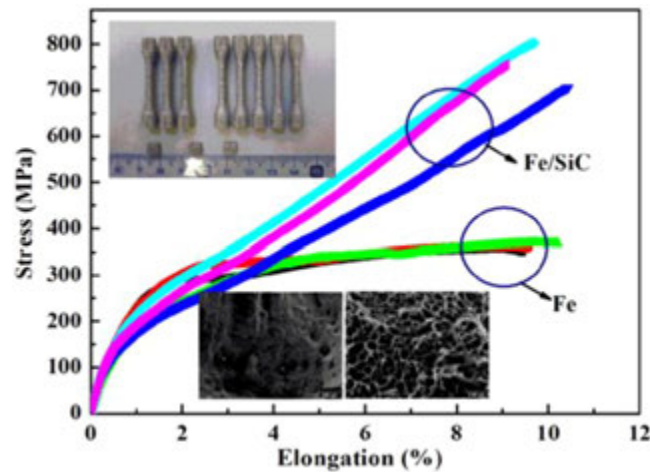


Fig. 21 Tensile properties of SLM processed SiC/Fe composite reported by (Song *et al.*). Reproduced from Song, B., Dong, S., Coddet, C., 2014. Rapid in situ fabrication of Fe/SiC bulk nanocomposites by selective laser melting directly from a mixed powder of microsized Fe and SiC. Scripta Materialia 75. Available at: <https://doi.org/10.1016/j.scriptamat.2013.11.031>.

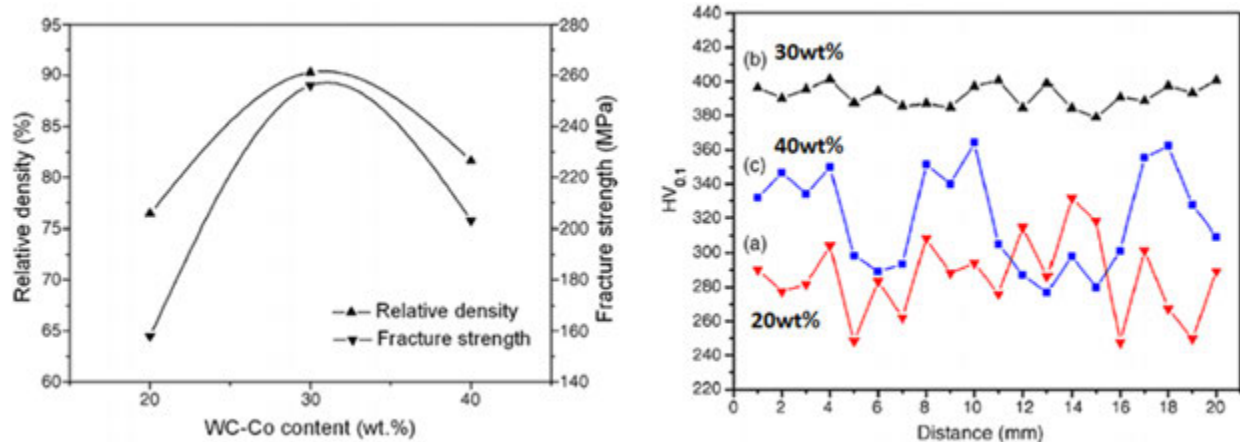
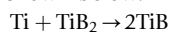


Fig. 22 Properties of AM fabricated WC-Co/Cu MMC reported by (Gu and Shen). Reproduced from Gu, D., Shen, Y., 2007. Influence of reinforcement weight fraction on microstructure and properties of submicron WC-Cop/Cu bulk MMCs prepared by direct laser sintering. Journal of Alloys and Compounds 431. Available at: <https://doi.org/10.1016/j.jallcom.2006.05.044>.

processing and properties of TiB reinforced Ti-Nb-Zr-Ta composites prepared from the blend of elemental Ti, Nb, Zr, and Ta powder with TiB₂ particles. Here, the TiB precipitates exhibited two different morphologies, submicron sized (coarser) hexagonal shape and nanosized (finer) needle shape. A better wear resistance was also reported for the TiB/Ti-Nb-Zr-Ta composite.

Hu and Cong, (2018); Hu and Ning (2018) also investigated the effects of laser power on the microstructural features of TiB/Ti composites prepared from an elemental blend of 98.4 wt%Ti and 1.6 wt% B powder via the LENS technique. While the laser power of 175 W produced the discontinuous network of fine TiB precipitates, a fully continuous network of very fine TiB particles was seen in the composites produced using 200 W laser power.

Attar *et al.* (2014a) used a powder mixture of α -Ti and TiB₂ to produce Ti based MMCs via selective laser melting method. In this study, the chemical reaction between Ti and TiB₂ results in the in-situ formation of needle shaped TiB particles in the Ti-matrix as shown below.



While the microstructural characterization results reported the distribution of much smaller sized TiB precipitates in the SLM processed composite when compared to its cast counterpart, the hardness and compressive properties were found to be similar (Attar *et al.*, 2014).

In a similar study (Attar *et al.*, 2015a), the same research group also investigated the influence of composite powder processing. The composites were from sets of powder: one milled for 2 h duration and the other milled for 4 h. While the use of 2 h milled powder produced more uniform powder deposition due to better sphericity of powders and associated flowability, the composites prepared from 4 h milled powder exhibited higher porosity levels. Also, the compressive properties were superior in case of the

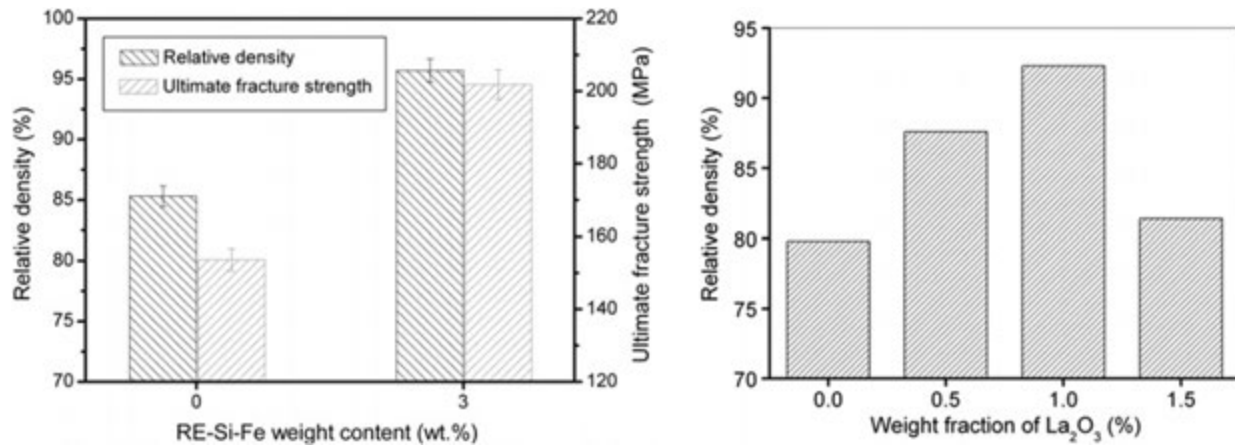


Fig. 23 Properties of AM fabricated RE and La₂O₃ added WC-Co/Cu MMCs reported by (Gu *et al.*; Gu and Shen). Reproduced from Gu, D., *et al.*, 2007. Effect of rare earth oxide addition on microstructures of ultra-fine WC-Co particulate reinforced Cu matrix composites prepared by direct laser sintering. *Materials Science and Engineering A* 445–446. Available at: <https://doi.org/10.1016/j.msea.2006.09.057>. Gu, D., Shen, Y., 2009b. Microstructures and properties of direct laser sintered tungsten carbide (WC) particle reinforced Cu matrix composites with RE - Si - Fe addition: A comparative study. *Journal of Materials Research* 24. Available at: <https://doi.org/10.1557/jmr.2009.0419>.

Table 1 Properties of TiB₂/AlSiMg AMCs reported by (Lorusso *et al.*)

Material	Microhardness	Loss of material ($\times 10^{-2} \text{ mm}^3/\text{m}$)
AlSi10Mg	97.6	0.9
AlSi10Mg + 10 wt% μ -TiB ₂	99.2	2.02
AlSi10Mg + 1 wt% nano-TiB ₂	97.5	0.7
AlSi10Mg (cast)	78	1.39

Note: Lorusso, M., *et al.*, 2016. Tribological behavior of aluminum alloy AlSi10Mg-TiB₂ composites produced by direct metal laser sintering (DMLS). *Journal of Materials Engineering and Performance* 25. Available at: <https://doi.org/10.1007/s11665-016-2190-5>.

Table 2 Tensile properties of AlSi10Mg MMCs reported by (Aversa *et al.*)

Composition	Porosity	Young's modulus (GPa)	Yield strength (MPa)	Ultimate strength (MPa)	Ductility (%)
AlSi10Mg	0.4	72.3 $\pm$ 2.6	255 $\pm$ 1	383 $\pm$ 2	6.7 $\pm$ 0.2
AlSi10Mg + 1 wt% nano-TiB ₂	0.8	74.6 $\pm$ 0.8	161 $\pm$ 2	289 $\pm$ 2	8.5 $\pm$ 0.6
AlSi10Mg + 10 wt% micro-TiB ₂	2.0	83.6 $\pm$ 1.5	188 $\pm$ 5	318 $\pm$ 10	8.5 $\pm$ 1.8
AlSi10Mg + 0.5 wt% nano-MgAl ₂ O ₄	0.7	73.1 $\pm$ 1.7	198 $\pm$ 1	327 $\pm$ 2	8.3 $\pm$ 0.8

Note: Aversa, A., *et al.*, 2017. Microstructural and mechanical characterization of aluminum matrix composites produced by laser powder bed fusion. *Advanced Engineering Materials* 19. Available at: <https://doi.org/10.1002/adem.201700180>.

composite made using 2 h milled powder. The results of nano-indentation also showed better nanohardness and elastic modulus (Attar *et al.*, 2017).

In a similar study, (Kang *et al.*, 2016) used pure Ti and CrB₂ powder in the SLM process to fabricate Ti composites with in-situ TiB particles exhibiting better microhardness and wear resistance.

Recently, Chen *et al.* (2017) evaluated the wet corrosion properties of TiB/Ti composites using electrochemical measurements in Hank's solution at body temperature. The results showed a broader passive region and a better corrosion resistance due to the presence of TiB, and unmelted TiB₂ particles which acted as micro cathodes forming multiple galvanic couple with α -Ti matrix serving as anode.

In a latest study, (Xia *et al.*, 2017) SLM processed a ball-milled composite mixture of (TiC + B₄C). Here, the reaction between Ti and B₄C particles resulted in the in-situ formation of whisker and granular like TiB and TiC precipitates, which were evenly distributed in the α -Ti matrix to impart hardness and strength. Also, the increasing energy density in this case contributed towards larger TiB and TiC phases.

Table 3 Mechanical properties of LENS processed TiC reinforced Ti composites

Material	Hardness (HV)	Yield strength (MPa)	Ultimate strength (MPa)	Elongation (%)
Pure Ti	260	520	585	19
Ti + 10 vol% TiC	301	520	575	2.5
Ti + 20 vol% TiC	336	515	590	1.5
Ti + 40 vol% TiC	503	–	–	–
Ti64	320–394	907	956	10.8
Ti + 8 vol% TiC	–	1041	1075	0.3

Note: Liu, W., DuPont, J.N., 2003. Fabrication of functionally graded TiC/Ti composites by laser engineered net shaping. Scripta Materialia 48. Available at: [https://doi.org/10.1016/S1359-6462\(03\)00020-4](https://doi.org/10.1016/S1359-6462(03)00020-4). Wang, F., et al., 2007. Laser fabrication of Ti6Al4V/TiC composites using simultaneous powder and wire feed. Materials Science and Engineering A 445–446. Available at: <https://doi.org/10.1016/j.msea.2006.09.093>. Zhang, Y., et al., 2008. Characterization of laser powder deposited Ti-TiC composites and functional gradient materials. Journal of Materials Processing Technology 206. Available at: <https://doi.org/10.1016/j.jmatprotec.2007.12.055>.

Table 4 Properties of insitu Ti + 8.3 vol% TiB composites

Condition	Yield strength (MPa)	Ultimate strength (MPa)	Elongation (%)
Powder ball milled for 2 h	1103	1421	17.8
Powder ball milled for 4 h	779	883	5.5
Composite with 10% porosity	767	868	5
Composite with 17% porosity	588	640	4
Composite with 37% porosity	234	256	2

Note: Attar, H., et al., 2014b. Selective laser melting of in situ titanium-titanium boride composites: Processing, microstructure and mechanical properties. Acta Materialia Available at: <https://doi.org/10.1016/j.actamat.2014.05.022>. Attar, H., et al., 2015a. Effect of powder particle shape on the properties of in situ Ti-TiB composite materials produced by selective laser melting. Journal of Materials Science and Technology 31. Available at: <https://doi.org/10.1016/j.jmst.2015.08.007>. Attar, H., et al., 2015b. Mechanical behavior of porous commercially pure Ti and Ti-TiB composite materials manufactured by selective laser melting. Materials Science and Engineering A 625, 350–356. Available at: <https://doi.org/10.1016/j.msea.2014.12.036>. Attar, H., et al., 2017. Nanoindentation and wear properties of Ti and Ti-TiB composite materials produced by selective laser melting. Materials Science and Engineering A 688, 20–26. Available at: <https://doi.org/10.1016/j.msea.2017.01.096>.

Using the LENS process, Balla et al. (2012) produced TiN reinforced Ti- composites with varying TiN amounts (5%–40%). The developed composites were investigated for their in-vitro wear resistance and biocompatibility. The results highlighted their suitability as potential wear resistant coatings for load bearing biomedical implants.

Recently, Das et al. (2012), (2014) fabricated (TiB + TiN) reinforced Ti-composite coatings using Ti64 matrix and varying amounts of BN powder via the LENS process. Here, the increase in BN content and the laser energy resulted in increasing amount of TiB and TiN precipitates for better hardness, Young's modulus and wear resistance compared to the Ti64 base alloy. Similarly, in a recent study Himanshu and coworkers (Sahasrabudhe et al., 2015, 2016) reported the in-situ formation of TiN and Ti₂N phases during the remelting of Ti substrate in nitrogen rich atmosphere to produce nitride rich composite coatings with better micro-hardness and wear resistance.

Additive Manufacturing of Nickel Based Metal Matrix Composites

Nickels based alloys are widely used in aerospace, power generation, marine and petrochemical industries. (Li et al., 2009; Liu et al., 2010) used the direct laser fabrication technique to produce pure Ni based composites containing upto 60 vol%. TiC wherein the increasing the amounts of TiC improved the hardness and wear resistance. Cooper et al. (2013) investigated the effects of ceramic reinforcements such as Al₂O₃, SiC, TiC on the properties of Inconel superalloy. The results showed mechanical properties betterment due to SiC and TiC reinforcements, although prominent cracking issues were seen in SiC reinforced composites. However, the addition of Al₂O₃ had no appreciable effects.

In a similar study, Hong et al. (2015a) studied the laser energy effects on the properties of ultrafine TiC particle reinforced IN625 composites. While the laser energy of 33 KJ/m lowered the densification behavior due to insufficient melting and residual porosities, the energy input above 100 KJ/m produced near dense composites with uniformly distributed ultrafine and smooth TiC reinforcements. Similarly, the mechanical property characterization results revealed enhanced strength and reduced wear rate due to significant grain refinement. However, the energy input of 160KJ/m caused coarsening of primary columnar dendrites due to excessive thermal energy input. Similar results were also reported by (Cao and Gu, 2015; Cao et al., 2017) in which the columnar dendrites were transformed into cellular structures by varying the ratio between temperature gradient and the solidification velocity. In a similar study, Zheng et al. (2010) reported the positive influence of Ni coating on the flowability of TiC particles leading to better interfacial integrity.

Table 5 Properties of AM processed Fe-MMCs

Materials	Microhardness	Wear rate (mm ³ /Nm)
Pure 316 L	220 HV _{0.1}	9.865×10^{-4}
316 L + 2.5TiB ₂ (mixed)	300 HV _{0.1}	–
316 L + 2.5TiB ₂ (ball milled)	300 HV _{0.1}	6.276×10^{-4}
316 L + 5vol%TiB ₂ (ball milled)	320 HV _{0.1}	4.489×10^{-4}
316 L + 10vol%TiB ₂ (ball milled)	600 HV _{0.1}	0.744×10^{-4}
316 L + 15TiB ₂ (mixed)	570 HV _{0.1}	0.0055×10^{-4}
316 L + 15vol%TiB ₂ (ball milled)	610 HV _{0.1}	0.0019×10^{-4}
316 L + 15vol%TiB ₂ (ball milled, HIP 1) ^a	310 HV _{0.1}	0.992×10^{-4}
316 L + 15vol%TiB ₂ (ball milled, HIP 2) ^b	420 HV _{0.1}	1.613×10^{-4}
316 L + 2.5 vol% micro-TiC (ball milled)	290 HV _{0.2}	9.696×10^{-4}
316 L + 2.5 vol% nano-TiC (ball milled)	290 HV _{0.2}	9.431×10^{-4}
316 L + 5 vol% micro-TiC (ball milled)	310 HV _{0.2}	8.573×10^{-4}
316 L + 5 vol% nano-TiC (ball milled)	310 HV _{0.2}	7.770×10^{-4}
316 L + 10 vol% micro-TiC (ball milled)	335 HV _{0.2}	7.338×10^{-4}
316 L + 10 vol% nano-TiC (ball milled)	365 HV _{0.2}	4.304×10^{-4}
316 L + 15 vol% micro-TiC (ball milled)	390 HV _{0.2}	3.555×10^{-4}
316 L + 15 vol% nano-TiC (ball milled)	405 HV _{0.2}	3.106×10^{-4}
H13	748 HV _{0.2}	22.6×10^{-6}
H13 + 15 vol% TiB ₂ (ball milled)	759 HV _{0.2}	1.268×10^{-6}
H13 + 15 vol% TiB ₂ (ball milled, after HIP 1) ^a	834 HV _{0.2}	1.96×10^{-6}

^aHIP 1: HIP at 1150°C, 207 MPa for 2 h, followed by rapid cooling to 200°C at 100°C/min.

^bHIP 2: HIP at 1150°C, 207 MPa for 2 h, followed by rapid cooling to 900°C at 50°C/min and held for 2 h, followed by rapid cooling to 200°C at 100°C/min.

Note: Almangour, B., Grzesiak, D., Yang, J.-M., 2016a. Selective laser melting of TiC reinforced 316L stainless steel matrix nanocomposites: Influence of starting TiC particle size and volume content. *Materials and Design* 104, 141–151. Available at: <https://doi.org/10.1016/j.matdes.2016.05.018>. Almangour, B., Grzesiak, D., Yang, J.M., 2016b. Rapid fabrication of bulk-form TiB₂/316L stainless steel nanocomposites with novel reinforcement architecture and improved performance by selective laser melting. *Journal of Alloys and Compounds* 680, 480–493. Available at: <https://doi.org/10.1016/j.jallcom.2016.04.156>. Almangour, B., Grzesiak, D., Yang, J.M., 2016c. Nanocrystalline TiC-reinforced H13 steel matrix nanocomposites fabricated by selective laser melting. *Materials and Design* 96, 150–161. Available at: <https://doi.org/10.1016/j.matdes.2016.02.022>. Almangour, B., Grzesiak, D., Yang, J.M., 2017b. Selective laser melting of TiB₂/316L stainless steel composites: The roles of powder preparation and hot isostatic pressing post-treatment. *Powder Technology* 309, 37–48. Available at: <https://doi.org/10.1016/j.powtec.2016.12.073>. Almangour, B., Grzesiak, D., Yang, J.M., 2017a. Scanning strategies for texture and anisotropy tailoring during selective laser melting of TiC/316L stainless steel nanocomposites. *Journal of Alloys and Compounds* 728, 424–435. Available at: <https://doi.org/10.1016/j.jallcom.2017.08.022>.

Hong *et al.* (2015b) also reported an improvement in the high temperature oxidation resistance of TiC/IN625 composites due to the combined presence of TiO₂ and Cr₂O₃ phases while the oxidized surface of IN625 was composed of just Cr₂O₃ precipitates. However, the oxidation attack increased at service temperatures beyond 800°C due to unfavorable oxidation of Cr₂O₃ to CrO₃.

Functionally graded IN690 composites reinforced with TiC particles were prepared by laser deposition (Wilson and Shin, 2012). In this study, the increasing amounts of TiC particles upto 30 vol% refined the matrix microstructure without getting dissolved at high temperatures. Using the method of selective laser melting, BN particles reinforced IN718 composites were also fabricated by (Kim *et al.*, 2017) and the results showed improvement in mechanical properties and thermal resistance upon BN addition.

TiC particles reinforced IN718 composites were also fabricated and the effects of laser energy density on the densification, microstructure and mechanical properties were studied (Hong *et al.*, 2013; Gu *et al.*, 2014). While the use of 350 J/mm³ laser energy density produced a dense microstructure with large amounts of smooth TiC phases, the lower energy density of 280 J/mm³ caused significant porosity. On the other hand, an optimal energy level of energy density produced a coherent interfacial layer of (Ti,M)C phases of thickness 0.8–1.4 μm (Hong *et al.*, 2013). Shi *et al.* (2016) also confirmed these observations through simulations and experimental validations. Here, the variation in laser power significantly affected the microstructural evolution, the variation in scan speed showed negligible changes. While the combination of high laser power (150 W) and low scan speed (50 mm/s) produced a wide and shallow cross-sectioned melt pool, the combination of low laser power (75 W) and high scan speed (300 mm/s) was energy efficient in the z-direction. On the other hand, the combination of 150 W laser power and 100 mm/s scan speed produced sound metallurgical bonding between the tracks and layers.

In a similar study, Rong and Gu (2016) developed WC/Ni- composites with a graded interfacial layer structure of (W,M)C where M = Ni,Cr,Fe surrounded by a diffusion layer of (W,M)C where M = Ni,Cr,Fe,Nb at an optimal energy density of 242 J/m.

Additive Manufacturing of Ferrous Based Metal Matrix Composites

The feasibility of using AM techniques to fabricate TiC reinforced Fe- MMCs was first study by (Gård *et al.*, 2006). Significant thermal cracking was observed due to increasing thermal expansion coefficients upon TiC dissolution and subsequent FCC - BCC phase transformations. Although the lesser TiC content (30 wt%) produced crack free composites, porosity was significantly high.

Song *et al.* (2014) in a similar study employed the SLM method to fabricate SiC/Fe composite from the mixture containing micron sized Fe and SiC powders. However, the microstructural results showed the uniform distribution of nanosized SiC particles due to the dissolution and subsequent precipitation of SiC phases, along with needle shaped martensite and partial pearlite phases. The same authors also explored the influence of hybrid (micro + nano) SiC particle addition and reported significant improvement in mechanical properties compared to pure Fe processed using similar method (Song *et al.*, 2013).

In a similar study, (Wei *et al.*, 2015) SLM processed the nano-hydroxyapatite (HA) particles reinforced stainless steel composites with an aim of understanding the effects of reinforcement volume fraction and the laser process parameters. It was observed that the high n-HA content resulted in significant particle clustering and cracks at melt pool boundaries which were improved upon increasing the laser scan speed. The superior mechanical properties of n-HA/SS composites reported in this study thus highlights the application potential as biomedical scaffolds. (Hao *et al.*, 2009) also developed HA reinforced 316 L composites using SLM. Here, since the reinforcement addition affected the laser energy input and the densification of bulk composites, the laser scanning procedure was duplicated to avoid balling effects and to facilitate better interfacial bonding.

Recently, (Almangour *et al.*, 2016b,c) employed the SLM method to fabricate SS composites containing different amounts of TiB₂ particles and reported that the optimum TiB₂ content of 10 vol% produced a homogeneous distribution of nano-ring like TiB₂ structures along the grain boundaries. The authors also investigated the influence of powder preparation and found that the particle size got significantly reduced after 8 h of ball milling (Almangour *et al.*, 2017b). Also, the use of ball milled powder in the SLM process resulted in better mechanical properties and wear resistance when compared to the composites made with just-mixed powder. However, the HIP-post processing of bulk composites resulted in high temperature grain coarsening and associated strength loss. Similar observations were also reported by the same authors for the TiC particles reinforced 316 L SS composites made using the powders of different starting size (Almangour *et al.*, 2016a, 2017a).

In another study, the same authors investigated the properties of TiB₂/H13 steel nanocomposites where the powder raw materials were ball milled prior to ball-milling (Almangour *et al.*, 2017c). Here, the microstructure of as-built nanocomposite was composed of very fine equiaxed grains and homogeneously dispersed TiB₂ particles within the grains and along the grain boundaries. The mechanical properties results showed better strength and hardness compared to unreinforced H13 base alloy. A further enhancement in hardness was reported post HIP-treatment. Similar results were also reported for TiC/H13 nanocomposites. (Almangour *et al.*, 2016b,c).

Additive Manufacturing of Copper Based Metal Matrix Composites

Copper based MMCs find excessive applications in electronics and semiconductor packaging. This section reviews the attempts made so far on the additive manufacturing of copper-based metal matrix composites. Tungsten has been widely used as the reinforcement in Cu-MMCs. Gu and Shen (2008) used the DMLS technique to consolidate the mixture of W + Cu powders and reported that the increase in elemental Cu content up to 60% resulted in a better densification due to increased liquid content. However, a further increase affected the melt pool stability to cause significant balling.

In a similar study, Gu and co-workers (Gu and Shen (2006), (2007), 2009a; Gu *et al.* (2008) processed the WC-Co/Cu composites using the laser sintering technique to understand the effects of laser energy input in terms of laser power, scan speed, layer thickness and hatch spacing. While the combination of laser power more than 400 W and scan speed greater than 0.06 m/s resulted in balling, a better densification was achieved for energy densities 0.16 and 0.23 KJ/mm³. Similarly, the reinforcement distribution was found uniform only when a minimum scan speed of 0.4 m/s and a maximum layer thickness of 0.3 mm were used for laser power less than 700 W (Gu *et al.*, 2008).

The same authors also investigated the effect of reinforcement (WC-Co particles) content and reported that the addition of 30 wt% reinforcement resulted in superior hardness of bulk composites due to improved reinforcement distribution and interfacial integrity (Gu and Shen, 2007). On the other hand, while the lower amounts of 20 wt% reinforcement caused severe balling due to melt-pool superheating, significant particle cluster due to poor melting and associated higher matrix' viscosity was recorded for higher amounts of 40 wt% reinforcement. The microstructural results also report two distinct reinforcement morphology: (1) partially dissolved – smooth and (2) completely dissolved – refine structures (Gu and Shen, 2007; Gu *et al.*, 2008).

Gu and Shen (2009b) also reported that the addition of 5 wt% RE-Si-Fe resulted in a better densification and the uniform distribution of WC reinforcement particles in WC-Co/Cu composites to contribute towards mechanical properties improvement. In a similarly study (Gu *et al.*, 2007), the same authors investigated the effects of 1 wt% La₂O₃ addition and reported an improvement in the relative density of bulk composites by 11.5% alongside microstructural refinement due to better distribution of the reinforcement phases. The same was attributed to the reduction in the melt pool surface tension and increased particle stimulated nucleation and further resistance to grain growth.

Lu *et al.* (2000) processed the elemental mixtures of Cu-Ti-C and Cu-Ni-Ti-C in a CO₂ laser assisted AM process to produce respective MMCs. While the in-situ formation of TiC phases was common for both the cases, a refined microstructure with better surface characteristics was reported for the Cu-Ni-T-C composites. In a similar study, Bhat *et al.* (2011) fabricated CNT reinforced Cu-10Sn alloy using a high energy laser where the addition of CNTs improved the mechanical and thermal properties. However, significant damage to CNT were also reported in this study.

Summary and Recommendations

In this article, the research progress on the additive manufacturing of metal matrix composites is summarized. The review of available literature suggests that only a selected few reinforcements such as SiC, TiC, TiB, TiB₂, BN, Al₂O₃ and to some extent in-situ developed compounds have been used repeatedly in most of the metal alloy matrices, although there are several hard and strong ceramic/metallic reinforcements found to be suitable. Recently, there were also few attempts made to fabricate CNT reinforced Al and Ti matrix composites. However, the CNTs were damaged upon interaction with the high energy laser source.

It was also found that the end properties of additively manufactured MMCs such as hardness, strength and wear resistance are generally superior than that of the unreinforced matrix alloy and in most cases, the processing condition along with the type and volume fraction of reinforcement played a significant role in the densification, microstructure and mechanical properties of additively manufactured MMCs. However, other properties such as high temperature mechanical properties, fatigue and creep require extensive attention. Currently, there are two simultaneous research approaches practiced in metal additive manufacturing: (1) on the pre-/ post-processing front and the other (2) on the actual AM processing methods.

While there has been a significant progress on the heat treatment of metallic alloys and metal matrix composite materials in general, literatures specifically applied to additively manufactured composites are meager and most of them are residual stress relaxation and age hardening related. Similarly, there has been some interest in the development of new materials that can be processed in commercial AM machines. On the other hand, the production of defect free powders and the development of stringent qualification norms are emerging. However, the AM methods are so far successful in producing dense parts through the optimization of process parameter window although the raw material powders do not fully comply with the process requirements. Similarly, the pre-processing of powder precursors through ball milling or mechanical alloying also receive extensive attention with regards to AM of MMCs.

With respect to processing, the feasibility and efficiency of specific AM processes receive great research interest. Although multiple studies have focused on the influence of print process parameters, extensive research efforts are required to deduce a deeper knowledge on microstructural evolution and the structure-property relationships. Especially, the size effects relating the test coupon properties with that of the actual parts and intricate features such as lattice structures need further research attention. In addition, advanced materials design and analysis tools are also needed to completely exploit the potential of AM process for greater industrial adoption.

Some of the critical challenges faced can be summarized as follows: (1) pre-processing of composite powder mixture: It is essential to prepare the composite powder mixture with required particle size and shape distribution as they cannot be readily obtained from the market, (2) unstable melt pool due to larger difference between the melting points of matrix and reinforcement material, (3) processing defects such as cracks and residual porosity due to poor densification and solidification conditions, and (4) need for post processing heat treatment due to faster cooling rates and the Young's moduli difference resulting in larger thermal residual stresses.

Despite these limitations, additive manufacturing of MMCs provide multiple benefits in terms of design flexibility and materials processing. Hence the development of AM composite technologies requires adequate attention to ensure process reliability and applicability.

References

- 3DEO, 2018. Metal 3D Printing Processes - Metal Extrusion FFF/FDM, 3DEO. Available at: <https://news.3deo.co/metal-3d-printing-processes-fdm-fff> (Accessed: 01.10.2019).
- Almangour, B., Grzesiak, D., Yang, J.-M., 2016a. Selective laser melting of TiC reinforced 316L stainless steel matrix nanocomposites: Influence of starting TiC particle size and volume content. *Materials and Design* 104, 141–151. <https://doi.org/10.1016/j.matdes.2016.05.018>.
- Almangour, B., Grzesiak, D., Yang, J.M., 2016b. Rapid fabrication of bulk-form TiB₂/316L stainless steel nanocomposites with novel reinforcement architecture and improved performance by selective laser melting. *Journal of Alloys and Compounds* 680, 480–493. <https://doi.org/10.1016/j.jallcom.2016.04.156>.
- Almangour, B., Grzesiak, D., Yang, J.M., 2016c. Nanocrystalline TiC-reinforced H13 steel matrix nanocomposites fabricated by selective laser melting. *Materials and Design* 96, 150–161. <https://doi.org/10.1016/j.matdes.2016.02.022>.
- Almangour, B., Grzesiak, D., Yang, J.M., 2017a. Scanning strategies for texture and anisotropy tailoring during selective laser melting of TiC/316L stainless steel nanocomposites. *Journal of Alloys and Compounds* 728, 424–435. <https://doi.org/10.1016/j.jallcom.2017.08.022>.
- Almangour, B., Grzesiak, D., Yang, J.M., 2017b. Selective laser melting of TiB₂/316L stainless steel composites: The roles of powder preparation and hot isostatic pressing post-treatment. *Powder Technology* 309, 37–48. <https://doi.org/10.1016/j.powtec.2016.12.073>.
- Almangour, B., Grzesiak, D., Yang, J.M., 2017c. Selective laser melting of TiB₂/H13 steel nanocomposites: Influence of hot isostatic pressing post-treatment. *Journal of Materials Processing Technology* 244, 344–353. <https://doi.org/10.1016/j.jmatprotec.2017.01.019>.
- Anandkumar, R., Almeida, A., Vilar, R., 2011. Wear behavior of Al-12Si/TiB₂ coatings produced by laser cladding. *Surface and Coatings Technology* 205. <https://doi.org/10.1016/j.surfcoat.2011.01.048>.
- Antony, A.A., 2012. Microstructure, Texture and Mechanical Property Evolution During Additive Manufacturing of Ti6Al4V Alloy for Aerospace Applications. The University of Manchester. (316).
- Attar, H., *et al.*, 2014. Comparative study of microstructures and mechanical properties of in situ Ti-TiB composites produced by selective laser melting, powder metallurgy, and casting technologies. *Journal of Materials Research* 29 (17), 1941–1950. <https://doi.org/10.1557/jmr.2014.122>.
- Attar, H., *et al.*, 2015a. Effect of powder particle shape on the properties of in situ Ti-TiB composite materials produced by selective laser melting. *Journal of Materials Science and Technology* 31. <https://doi.org/10.1016/j.jmst.2015.08.007>.
- Attar, H., *et al.*, 2017. Nanoindentation and wear properties of Ti and Ti-TiB composite materials produced by selective laser melting. *Materials Science and Engineering A* 688, 20–26. <https://doi.org/10.1016/j.msea.2017.01.096>.

- Attar, H., *et al.*, 2014a. Selective laser melting of in situ titanium-titanium boride composites: Processing, microstructure and mechanical properties. *Acta Materialia* 76. <https://doi.org/10.1016/j.actamat.2014.05.022>.
- Aversa, A., *et al.*, 2017. Microstructural and mechanical characterization of aluminum matrix composites produced by laser powder bed fusion. *Advanced Engineering Materials* 19. <https://doi.org/10.1002/adem.201700180>.
- Balla, V.K., *et al.*, 2012. Laser processed TiN reinforced Ti6Al4V composite coatings. *Journal of the Mechanical Behavior of Biomedical Materials* 6. <https://doi.org/10.1016/j.jmbbm.2011.09.007>.
- Banerjee, R., *et al.*, 2005. Nanoscale TiB precipitates in laser deposited Ti-matrix composites. *Scripta Materialia* 53. <https://doi.org/10.1016/j.scriptamat.2005.08.014>.
- Bhat, A., *et al.*, 2011. Carbon nanotube reinforced Cu-10Sn alloy composites: Mechanical and thermal properties. *Materials Science and Engineering A* 528. <https://doi.org/10.1016/j.msea.2011.05.038>.
- Cao, S., Gu, D., 2015. Laser metal deposition additive manufacturing of TiC/Inconel 625 nanocomposites: Relation of densification, microstructures and performance. *Journal of Materials Research* 30. <https://doi.org/10.1557/jmr.2015.358>.
- Cao, S., Gu, D., Shi, Q., 2017. Relation of microstructure, microhardness and underlying thermodynamics in molten pools of laser melting deposition processed TiC/Inconel 625 composites. *Journal of Alloys and Compounds* 692. <https://doi.org/10.1016/j.jallcom.2016.09.098>.
- Chang, F., *et al.*, 2015. Selective laser melting of in-situ Al₄SiC₄ + SiC hybrid reinforced Al matrix composites: Influence of starting SiC particle size. *Surface and Coatings Technology* 272, 15–24. <https://doi.org/10.1016/j.surfcoat.2015.04.029>.
- Chen, Y., *et al.*, 2017. Corrosion behaviour of selective laser melted Ti-TiB biocomposite in simulated body fluid. *Electrochimica Acta* 232. <https://doi.org/10.1016/j.electacta.2017.02.112>.
- Cooper, D.E., *et al.*, 2013. Additive layer manufacture of Inconel 625 metal matrix composites, reinforcement material evaluation. *Journal of Materials Processing Technology* 213. <https://doi.org/10.1016/j.jmatprotec.2013.06.021>.
- Dadbakhsh, S., Hao, L., 2014. Effect of layer thickness in selective laser melting on microstructure of Al/5 wt%Fe₂O₃ powder consolidated parts. *The Scientific World Journal* 2014. <https://doi.org/10.1155/2014/106129>.
- Das, M., *et al.*, 2012. Laser processing of in situ synthesized TiB-TiN-reinforced Ti6Al4V alloy coatings. *Scripta Materialia* 66. <https://doi.org/10.1016/j.scriptamat.2012.01.010>.
- Das, M., *et al.*, 2014. In situ synthesized TiB-TiN reinforced Ti6Al4V alloy composite coatings: Microstructure, tribological and in-vitro biocompatibility. *Journal of the Mechanical Behavior of Biomedical Materials* 29. <https://doi.org/10.1016/j.jmbbm.2013.09.006>.
- Domack, M.S., Baughman, J.M., 2005. Development of nickel-titanium graded composition components. *Rapid Prototyping Journal* 11 (1), 41–51. <https://doi.org/10.1108/13552540510573383>.
- Famodimu, O.H., 2016. Additive Manufacturing of Aluminium-Metal Matrix Composite Developed Through Mechanical Alloying. University of Wolverhampton. (Available at: <http://hdl.handle.net/2436/620337>).
- Gård, A., Krakhmalev, P., Bergström, J., 2006. Microstructural characterization and wear behavior of (Fe,Ni)-TiC MMC prepared by DMLS. *Journal of Alloys and Compounds* 421. <https://doi.org/10.1016/j.jallcom.2005.09.084>.
- Ghosh, S.K., Saha, P., 2011. Crack and wear behavior of SiC particulate reinforced aluminium based metal matrix composite fabricated by direct metal laser sintering process. *Materials and Design* 32. <https://doi.org/10.1016/j.matdes.2010.06.020>.
- Ghosh, S.K., Saha, P., Kishore, S., 2010. Influence of size and volume fraction of SiC particulates on properties of ex situ reinforced Al-4.5Cu-3Mg metal matrix composite prepared by direct metal laser sintering process. *Materials Science and Engineering A* 527. <https://doi.org/10.1016/j.msea.2010.03.108>.
- Gibson, I., Rosen, David, W., Stucker, B., 2010a. Additive manufacturing technologies. Development. 1–27. <https://doi.org/10.1007/978-1-4419-1120-9>.
- Gibson, I., Rosen, D.W., Stucker, B., 2010. Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing. Springer. pp. 17–40.
- Gu, D., *et al.*, 2007. Effect of rare earth oxide addition on microstructures of ultra-fine WC-Co particulate reinforced Cu matrix composites prepared by direct laser sintering. *Materials Science and Engineering A* 445–446. <https://doi.org/10.1016/j.msea.2006.09.057>.
- Gu, D., *et al.*, 2009. In-situ TiC particle reinforced Ti-Al matrix composites: Powder preparation by mechanical alloying and selective laser melting behavior. *Applied Surface Science* 255. <https://doi.org/10.1016/j.apsusc.2009.07.008>.
- Gu, D., *et al.*, 2011. Nanocrystalline TiC reinforced Ti matrix bulk-form nanocomposites by selective laser melting (SLM): Densification, growth mechanism and wear behavior. *Composites Science and Technology* 71. <https://doi.org/10.1016/j.compscitech.2011.07.010>.
- Gu, D., *et al.*, 2012. Selective laser melting of TiC/Ti bulk nanocomposites: Influence of nanoscale reinforcement. *Scripta Materialia* 67. <https://doi.org/10.1016/j.scriptamat.2012.04.013>.
- Gu, D., *et al.*, 2014. Combined strengthening of multi-phase and graded interface in laser additive manufactured TiC/Inconel 718 composites. *Journal of Physics D Applied Physics* 47. <https://doi.org/10.1088/0022-3727/47/4/045309>.
- Gu, D., *et al.*, 2015. Rapid fabrication of Al-based bulk-form nanocomposites with novel reinforcement and enhanced performance by selective laser melting. *Scripta Materialia* 96. <https://doi.org/10.1016/j.scriptamat.2014.10.011>.
- Gu, D., Shen, Y., 2006. WC-Co particulate reinforcing Cu matrix composites produced by direct laser sintering. *Materials Letters* 60. <https://doi.org/10.1016/j.matlet.2006.03.103>.
- Gu, D., Shen, Y., 2007. Influence of reinforcement weight fraction on microstructure and properties of submicron WC-Cop/Cu bulk MMCs prepared by direct laser sintering. *Journal of Alloys and Compounds* 431. <https://doi.org/10.1016/j.jallcom.2006.05.044>.
- Gu, D., Shen, Y., 2008. Influence of Cu-liquid content on densification and microstructure of direct laser sintered submicron W-Cu/micron Cu powder mixture. *Materials Science and Engineering A* 489. <https://doi.org/10.1016/j.msea.2007.12.008>.
- Gu, D., Shen, Y., 2009a. Effects of processing parameters on consolidation and microstructure of W-Cu components by DMLS. *Journal of Alloys and Compounds* 473. <https://doi.org/10.1016/j.jallcom.2008.05.065>.
- Gu, D., Shen, Y., 2009b. Microstructures and properties of direct laser sintered tungsten carbide (WC) particle reinforced Cu matrix composites with RE - Si - Fe addition: A comparative study. *Journal of Materials Research* 24. <https://doi.org/10.1557/jmr.2009.0419>.
- Gu, D., Shen, Y., Xiao, J., 2008. Influence of processing parameters on particulate dispersion in direct laser sintered WC-Co_p/Cu MMCs. *International Journal of Refractory Metals and Hard Materials* 26. <https://doi.org/10.1016/j.ijrmhm.2007.09.005>.
- Hao, L., *et al.*, 2009. Selective laser melting of a stainless steel and hydroxyapatite composite for load-bearing implant development. *Journal of Materials Processing Technology* 209. <https://doi.org/10.1016/j.jmatprotec.2009.06.012>.
- Hong, C., *et al.*, 2013. Laser metal deposition of TiC/Inconel 718 composites with tailored interfacial microstructures. *Optics and Laser Technology* 54. <https://doi.org/10.1016/j.optlastec.2013.05.011>.
- Hong, C., Gu, D., Dai, D., *et al.*, 2015a. Laser additive manufacturing of ultrafine TiC particle reinforced Inconel 625 based composite parts: Tailored microstructures and enhanced performance. *Materials Science and Engineering A* 635. <https://doi.org/10.1016/j.msea.2015.03.043>.
- Hong, C., Gu, D., Dai, D., *et al.*, 2015b. High-temperature oxidation performance and its mechanism of TiC/Inconel 625 composites prepared by laser metal deposition additive manufacturing. *Journal of Laser Applications* 27 (S1), (S17005). <https://doi.org/10.2351/1.4898647>.
- Hu, Y., Cong, W., 2018. Laser deposition-additive manufacturing of TiB-Ti composites with novel three-dimensional quasi-continuous network microstructure: Effects on strengthening and toughening. *Composites Part B: Engineering* 133. <https://doi.org/10.1016/j.compositesb.2017.09.019>.
- Hu, Y., Ning, F., 2018. Laser engineered net shaping of quasi-continuous network microstructural TiB reinforced titanium matrix bulk composites: Microstructure and wear performance. *Optics and Laser Technology* 99. <https://doi.org/10.1016/j.optlastec.2017.08.032>.

- Jue, J., Gu, D., 2017. Selective laser melting additive manufacturing of in situ Al₂Si₄O₁₀/Al composites: Microstructural characteristics and mechanical properties. *Journal of Composite Materials* 51. <https://doi.org/10.1177/0021998316649251>.
- Kainer, K.U., 2006. Basics of metal matrix composites. In: *Metal Matrix Composites: Custom-made Materials for Automotive and Aerospace Engineering*. <https://doi.org/10.1002/3527608117.ch1>.
- Kang, N., *et al.*, 2016. In-situ TiB/near α Ti matrix composites manufactured by selective laser melting. *Additive Manufacturing* 11. <https://doi.org/10.1016/j.addma.2016.04.001>.
- Karthik, G.M., *et al.*, 2017. Additive manufacturing of an aluminum matrix composite reinforced with nanocrystalline high-entropy alloy particles. *Materials Science and Engineering A* 679. <https://doi.org/10.1016/j.msea.2016.10.038>.
- Kim, S.H., *et al.*, 2017b. Thermo-mechanical improvement of Inconel 718 using ex situ boron nitride-reinforced composites processed by laser powder bed fusion. *Scientific Reports* 7. <https://doi.org/10.1038/s41598-017-14713-1>.
- Kun, C., *et al.*, 2017. The formation mechanism of TiC reinforcement and improved tensile strength in additive manufactured Ti matrix nanocomposite. *Vacuum* 143. <https://doi.org/10.1016/j.vacuum.2017.05.029>.
- Li, X.P., *et al.*, 2017b. Selective laser melting of nano-TiB₂decorated AlSi10Mg alloy with high fracture strength and ductility. *Acta Materialia* 129. <https://doi.org/10.1016/j.actamat.2017.02.062>.
- Li, Y., *et al.*, 2009. Effect of TiC content on Ni/TiC composites by direct laser fabrication. *Materials and Design* 30. <https://doi.org/10.1016/j.matdes.2008.06.046>.
- Liu, W., DuPont, J.N., 2003. Fabrication of functionally graded TiC/Ti composites by laser engineered net shaping. *Scripta Materialia* 48. [https://doi.org/10.1016/S1359-6462\(03\)00020-4](https://doi.org/10.1016/S1359-6462(03)00020-4).
- Liu, Z.-D., *et al.*, 2010. Microstructure and mechanical behaviors of in situ TiC particulates reinforced Ni matrix composites. *Materials Science and Engineering A* 527. <https://doi.org/10.1016/j.msea.2010.02.061>.
- Lorusso, M., *et al.*, 2016. Tribological behavior of aluminum alloy AlSi10Mg-TiB₂ composites produced by direct metal laser sintering (DMLS). *Journal of Materials Engineering and Performance* 25. <https://doi.org/10.1007/s11665-016-2190-5>.
- Lu, L., *et al.*, 2000. In situ formation of TiC composite using selective laser melting. *Materials Research Bulletin* 35. [https://doi.org/10.1016/S0025-5408\(00\)00339-1](https://doi.org/10.1016/S0025-5408(00)00339-1).
- Marchese, G., *et al.*, 2018. Development and characterisation of aluminium matrix nanocomposites AlSi10Mg/MgAl204 by laser powder bed fusion. *Metals* 8. <https://doi.org/10.3390/met8030175>.
- Nag, S., *et al.*, 2009. Characterization of novel borides in Ti-Nb-Zr-Ta + 2B metal-matrix composites. *Materials Characterization* 60. <https://doi.org/10.1016/j.matchar.2008.07.011>.
- Prashanth, K.G., *et al.*, 2016. Processing of Al-12Si-TNM composites by selective laser melting and evaluation of compressive and wear properties. *Journal of Materials Research* 31. <https://doi.org/10.1557/jmr.2015.326>.
- Rong, T., Gu, D., 2016. Formation of novel graded interface and its function on mechanical properties of WC-1-x reinforced Inconel 718 composites processed by selective laser melting. *Journal of Alloys and Compounds* 680. <https://doi.org/10.1016/j.jallcom.2016.04.107>.
- Sahasrabudhe, H., Soderlind, J., Bandyopadhyay, A., 2015. In situ nitridation of titanium using Lens™. In: Narayan, R., Bose, S., Bandyopadhyay, A. (Eds.), *Biomaterials Science: Processing, Properties and Applications V: Ceramic Transactions, Volume 254*. The American Ceramic Society. <https://doi.org/10.1002/9781119190134.ch14>.
- Sahasrabudhe, H., Soderlind, J., Bandyopadhyay, A., 2016. Laser processing of in situ TiN/Ti composite coating on titanium. *Journal of the Mechanical Behavior of Biomedical Materials* 53. <https://doi.org/10.1016/j.jmbbm.2015.08.013>.
- Samuel, S., *et al.*, 2008. Wear resistance of laser-deposited boride reinforced Ti-Nb-Zr-Ta alloy composites for orthopedic implants. *Materials Science and Engineering C* 28. <https://doi.org/10.1016/j.msec.2007.04.029>.
- Shi, Q., *et al.*, 2016. Effects of laser processing parameters on thermal behavior and melting/solidification mechanism during selective laser melting of TiC/Inconel 718 composites. *Optics and Laser Technology* 84. <https://doi.org/10.1016/j.optlastec.2016.04.009>.
- Song, B., *et al.*, 2013. Microstructure and tensile behavior of hybrid nano-micro SiC reinforced iron matrix composites produced by selective laser melting. *Journal of Alloys and Compounds* 579. <https://doi.org/10.1016/j.jallcom.2013.06.087>.
- Song, B., Dong, S., Coddet, C., 2014. Rapid in situ fabrication of Fe/SiC bulk nanocomposites by selective laser melting directly from a mixed powder of micro-sized Fe and SiC. *Scripta Materialia* 75. <https://doi.org/10.1016/j.scriptamat.2013.11.031>.
- Wang, F., *et al.*, 2007. Laser fabrication of Ti6Al4V/TiC composites using simultaneous powder and wire feed. *Materials Science and Engineering A* 445–446. <https://doi.org/10.1016/j.msea.2006.09.093>.
- Wang, L.Z., Chen, T., Wang, S., 2017. Microstructural characteristics and mechanical properties of carbon nanotube reinforced AlSi10Mg composites fabricated by selective laser melting. *Optik* 143. <https://doi.org/10.1016/j.ijleo.2017.06.086>.
- Wei, Q., *et al.*, 2015. Selective laser melting of stainless-steel/nano-hydroxyapatite composites for medical applications: Microstructure, element distribution, crack and mechanical properties. *Journal of Materials Processing Technology* 222. <https://doi.org/10.1016/j.jmatprotec.2015.02.010>.
- Wilson, J.M., Shin, Y.C., 2012. Microstructure and wear properties of laser-deposited functionally graded Inconel 690 reinforced with TiC. *Surface and Coatings Technology* 207. <https://doi.org/10.1016/j.surfcoat.2012.07.058>.
- Xia, M., *et al.*, 2017. Microstructure growth behavior and its evolution mechanism during laser additive manufacture of in-situ reinforced (TiB + TiC)/Ti composite. *Journal of Alloys and Compounds* 728. <https://doi.org/10.1016/j.jallcom.2017.09.033>.
- Zhang, Y., *et al.*, 2008. Characterization of laser powder deposited Ti-TiC composites and functional gradient materials. *Journal of Materials Processing Technology* 206. <https://doi.org/10.1016/j.jmatprotec.2007.12.055>.
- Zhao, X., *et al.*, 2016. Selective laser melting of carbon/AlSi10Mg composites: Microstructure, mechanical and electrical properties. *Journal of Alloys and Compounds* 665. <https://doi.org/10.1016/j.jallcom.2015.12.126>.
- Zhao, X., *et al.*, 2019. Microstructure characteristics and its formation mechanism of selective laser melting SiC reinforced Al-based composites. *Vacuum* 160. <https://doi.org/10.1016/j.vacuum.2018.11.022>.
- Zheng, B., *et al.*, 2010. The influence of Ni-coated TiC on laser-deposited IN625 metal matrix composites. *Metallurgical and Materials Transactions A* 41. <https://doi.org/10.1007/s11661-009-0126-5>.

Severe Plastic Deformation Processing of Metal Matrix Composites

Sankaranarayanan Seetharaman, National University of Singapore, Singapore

Ankita Mandal, Indian Institute of Technology, Delhi, India

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Grain size is a key microstructural factor that determines the mechanical properties of metallic materials. Among different metal working processes, methods involving grain refinement are promising for improved strength and fracture toughness. While grain refinement in conventional thermo-mechanical processes often leads to an average grain size in the order of few microns, severe plastic deformation (SPD) methods are capable of producing ultrafine or nanocrystalline microstructure (see Fig. 1) that offers multi-fold increase in strength properties.

SPD describes a group of metal-working processes that involve very large strains (von Mises strain in excess of 2) and complex stress states that result in large volumes of defect densities to generate nano-crystalline or ultrafine microstructure and the key feature is that the external dimensions of the workpiece do not change significantly. Unlike conventional metal working processes that follow a continuous strain path to result in a fibrous or cellular sub-grain structure with a large volume of low angle grain boundaries, SPD techniques offer possibility to change the strain path that promotes high angle boundaries and granular (sub) structures during deformation.

Presently, there are various SPD techniques applicable for bulk batch and continuous billets; for rods, plates, tubes, and sheet materials; for one-step and multi-step processing; and for SPD of surfaces and thin cross-sections. However, they are being carried out on a laboratory scale using small samples, simple tools, and labor-intensive procedures that do not meet industrial requirements. Therefore, their applicability to products, especially those with a complex shape and large size are limited.

Types of Severe Plastic Deformation Methods

Some of the examples of severe plastic deformation methods include: (1) equal channel angular processing or extrusion (ECAP), (2) high pressure torsion (HPT), (3) multi-axial forging (MAF), (4) accumulative roll bonding (ARB), and (5) repetitive corrugation and straightening (RCS). While ECAP, HPT, and MAF methods are applicable for bulk materials, ARB, and RCS are used for sheet metal processing.

Equal Channel Angular Pressing (ECAP)

ECAP is one of the most common SPD methods. It was originally invented by Segal in 1972 (Segal, 1999, 1974). This method is widely explored for manufacturing ultra-fine grained products including fasteners like screws and screw rivets commonly used in the assembly of aluminum components for aircraft and other structures, elements for aircraft fuselages, sections of various size and shape and sheets for assemblies operating in corrosive environments and at cryogenic temperatures, and complex-shaped parts produced by superplastic forming. This method improves the strength and ductility of metal matrix composites by means of grain refinement and favorable crystallographic texture modification. Fig. 2 shows an example of microstructural changes in SiC particles reinforced AZ91 composites after 16 pass ECAP performed using a 90° rotary die.

As schematically shown in Fig. 3, ECAP processing involves pressing or extrusion of the material through a die with identical inlet and outlet cross sections, intersecting at an angle " ϕ " that varies between 60 and 135°. Since the total strain imposed during ECAP determines the grain refinement, the channel angle is considered critical and most experimental works report the use of channel angles between 90 and 120°. When the fillet radius is zero, the work piece undergoes simple shear. Some of the ECAP procedures also involve a rounded corner with angle ψ . The plastic strain accumulated during ECAP processing can be calculated using Eq. (1) (Iwahashi *et al.*, 1996; Valiev *et al.*, 2006). Therefore, for $\phi = 90^\circ$ and $\psi = 0^\circ$, the equivalent plastic strain is 1.155.

$$\text{Plastic strain accumulated during ECAP, } \bar{\epsilon} = \left[\frac{2 \cot\left(\frac{\phi}{2} + \frac{\psi}{2}\right) + \psi \operatorname{cosec}\left(\frac{\phi}{2} + \frac{\psi}{2}\right)}{\sqrt{3}} \right] \quad (1)$$

Other significant factors that affect the strain accumulation and grain refinement during ECAP processing include pressing temperature, pressing speeds, the number of passes and rotation strategy. Fig. 4 shows the effects of inter-pass rotation schemes (Route A (no rotation), Route B (90° back and forth rotation between passes), Route C (180° rotation between passes)) on the microstructure of ECAP processed Mg-4Al-1Ca alloy. In general, the ECAP process is repeated for multiple times and the work piece is often rotated between passes in order to cause shearing on different planes. While the material volume gets restored to its initial shape after a specific number of passes (after every 2nd pass in route C and after 4th pass in Bc route), the strain path varies between ECAP passes and the changes depends on the die angle ϕ and the rotation angle φ . Here, the equivalent strain in

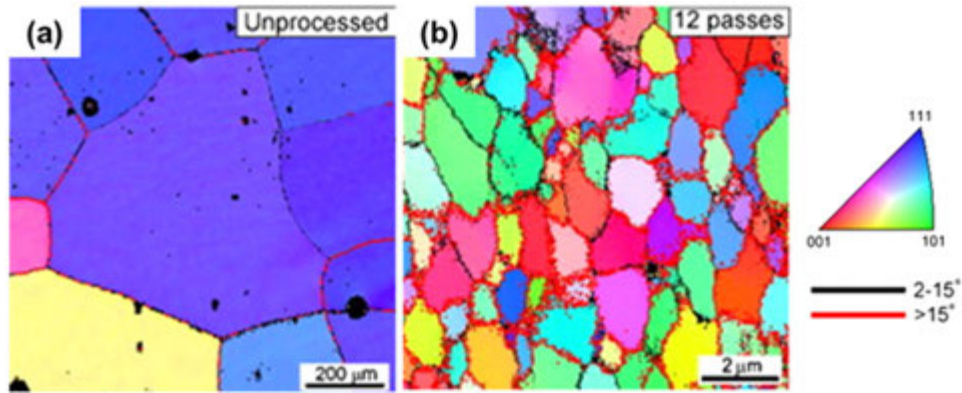


Fig. 1 Microstructure of high purity aluminum (a) before and (b) after severe plastic deformation processing. Adapted from Kawasaki, M., Horita, Z., Langdon, T.G., 2009. Microstructural evolution in high purity aluminum processed by ECAP. *Mater. Sci. Eng. A* doi:10.1016/j.msea.2009.06.032. The color of grains corresponds to the orientations as presented in the unit triangle and the grain boundaries denoted by black and red lines correspond to low ($2-15^\circ$) and high-angle ($>15^\circ$) misorientations.

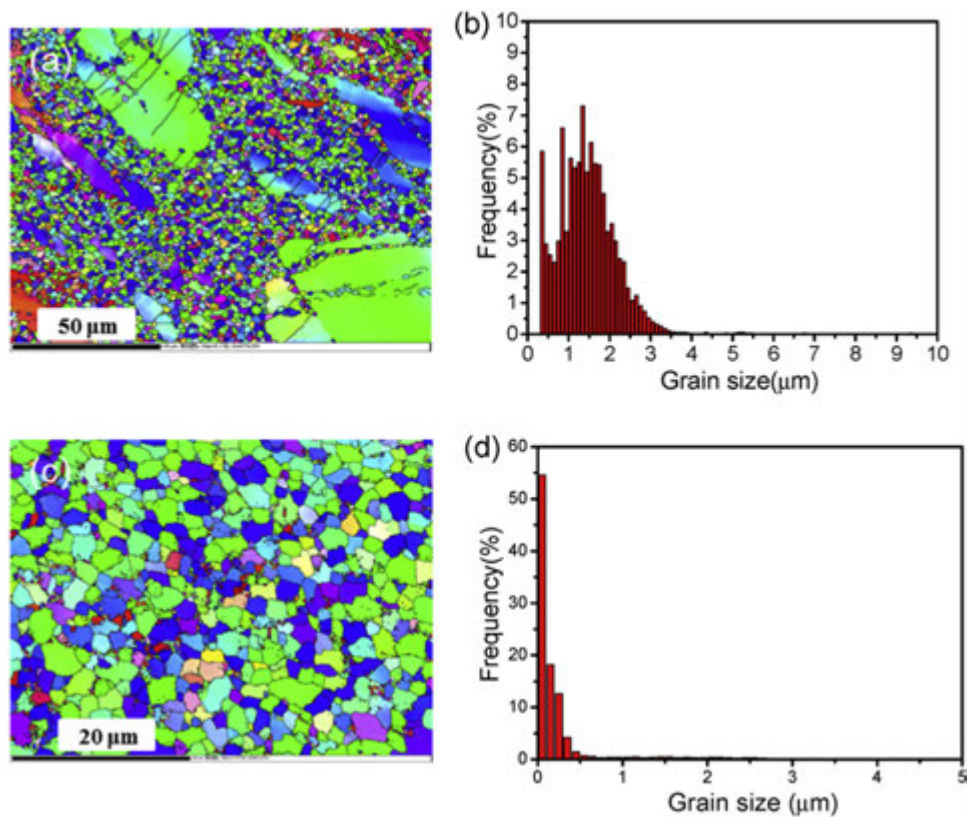


Fig. 2 IPF (a, c) and grain size (b, d) of ECAP processed $\text{SiC}_p/\text{AZ91}$. (a, b) 4P; (c, d) 16P. Adapted from Xu, Q., Ma, A., Saleh, B., *et al.*, 2020. Enhancement of strength and ductility of $\text{SiC}_p/\text{AZ91}$ composites by RD-ECAP processing. *Mater. Sci. Eng. A* 771, 138579. doi:10.1016/j.msea.2019.138579.

multiple pass processing can be calculated by multiplying the Eq. (1) by the number of passes. For example, while single pass with $\Phi = 90^\circ$ results in an equivalent strain of 1.155, four passes using Route Bc produce an overall strain ~ 4 to develop a fairly uniform grain structure over a range of alloys. Thus, it can be understood that the individual strain path plays an important role in controlling the strain accumulation, microstructural evolution and the end mechanical properties (Minárik *et al.*, 2017). In this regard, some of the recent literatures also highlight the requirement of strains greater than 6 to eliminate low angle grain boundaries and result in a finer grain size in the order of few to few hundred nanometers (Valiev *et al.*, 2000).

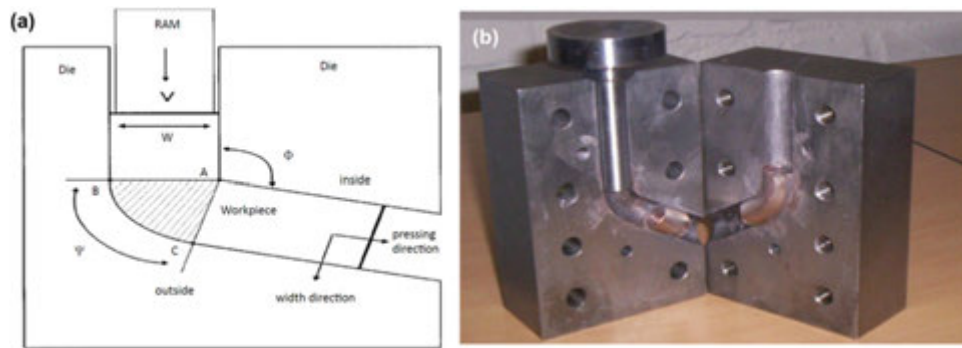


Fig. 3 (a) Schematic representation of ECAP process and (b) an ECAP die used to process copper alloy. Adapted from Ref. Sanusi, K.O., Makinde, O.D., Oliver, G.J., 2012. Equal channel angular pressing technique for the formation of ultra-fine grained structures. *S. Afr. J. Sci* 108, Article 212. doi:10.4102/sajs.v108i9/10.212.

Langdon *et al.* (2000) and Furukawa *et al.* (2000) showed that the level of grain refinement achieved by shear through 90° dies is significantly high when compared to die angles greater than 90°.

Despite the advantages as mentioned above, ECAP processing is mostly limited to laboratory scale as a substantial volume of material at the leading and trailing edge does not undergo large deformation. Similarly, the larger frictional stresses at the entrance of the die limits the work piece length. To reduce stress concentration, Segal *et al.* (1995) and Semiatin and DeLo (1999) modified the die design by moving the floor of the exit channel along with the work piece. Alternatively, Chakkingal *et al.* (1998) proposed pulling the work piece through a die as shown in Fig. 5. While the drawing operation eliminates the frictional force at the entrance of the die and reduced the overall metal forming force, one of the serious limitations is that the stress required to draw the material should not exceed the tensile strength.

High Pressure Torsion (HPT)

In high-pressure torsion (HPT), the material is subjected to severe plastic deformation by a simultaneous action of high pressure and torsional strain. A vertical pressure of around 5 GPa is applied to press down a small disk of the material (usually about 20 mm in diameter and about 0.2–0.5 mm in thickness) on the support and the plunger is then rotated to apply a torsional strain as shown in Fig. 6. Hence, the frictional force between the plunger and the sample, and the sample and the anvil, help to shear the material (Iwahashi *et al.*, 1996).

Here, the effective strain is given by:

$$\varepsilon_{\text{eff}} = \gamma / \sqrt{3} \quad (2)$$

where γ is the shear strain achieved for “N” number of turns which can be calculated as follows:

$$\gamma = \frac{2rN\pi}{l} \quad (3)$$

r and l are the radius and thickness of the disk, respectively.

From Eqs. (2) and (3), the shear strain increases with increasing radius, thus making the deformation inhomogeneous. However, existing literature highlights the fact that the microstructure tends to homogenize with increasing number of rotations as inferred from microhardness and grain size measurements (Valiev *et al.*, 2006). Therefore, the actual deformation in HPT is complex compared to classical torsion (see Fig. 7).

Multiaxial Forging (MAF)

Multiaxial forging (MAF) or compression (MAC) involves repeated uniaxial compression of materials, sequentially along the three orthogonal axes i.e., the loading direction is changed through 90° between successive compressions as shown in Fig. 8. Although this method can produce fine microstructures, it requires surface preparation unless a confined channel die that offers plane strain compression is used to produce a higher effective strain (for the same reduction in height) compared to uniaxial compression. While the open channel die has the limitation of non-uniform deformation due to bulging of free surfaces and early cracking, the confined channel die ensures no bulging and the sample conforms to the shape of the die after each pass resulting in more uniform deformation (Sanusi *et al.*, 2012).

Accumulated Roll Bonding (ARB)

It is a solid-state process originally invented by Tsuji *et al.* (1999) in 1999 to fabricate multi-layered composite structures. In this process, a stack of two sheets with equal thickness is subjected to plane strain rolling which binds them together and reduce the

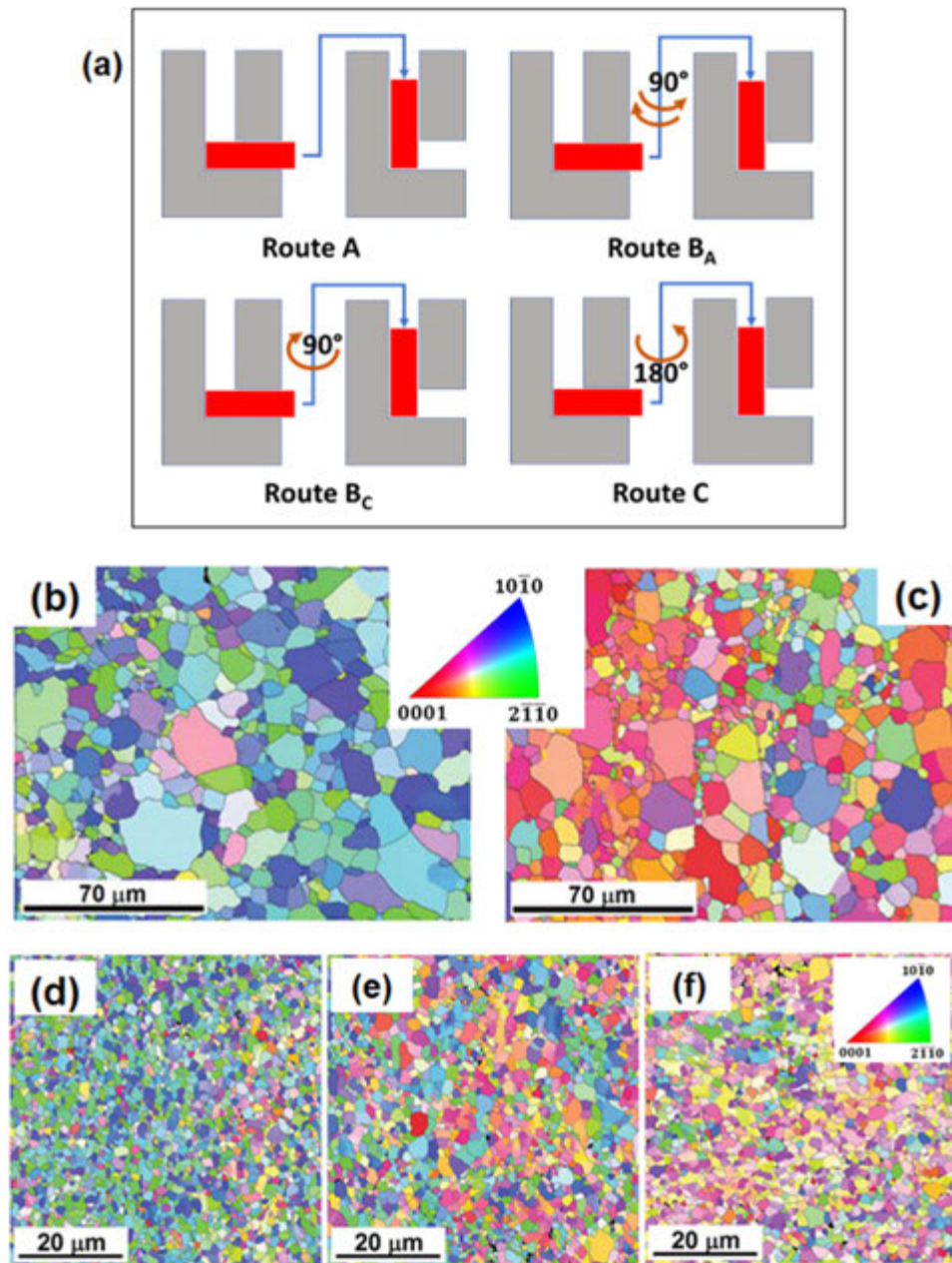


Fig. 4 (a) Schematic of ECAP routes. (b–c) Initial microstructure (IPF maps obtained on the (b) cross-section and (c) longitudinal section) of extruded Mg-4Al-1Ca alloy. Microstructure after 8 passes ECAP via (d) route A, (e) route B_C and (f) route C. Adapted from Refs. Sanusi, K.O., Makinde, O.D., Oliver, G.J., 2012. Equal channel angular pressing technique for the formation of ultra-fine grained structures. *S. Afr. J. Sci* 108, Article 212. doi:10.4102/sajs.v108i9/10.212. Minárik, P., Krajčák, T., Srba, O., *et al.*, 2017. Chapter 2 – Mechanical properties and microstructure development in ultrafine-grained materials processed by equal-channel angular pressing. In: Cabibbo, M. (Ed.), *Severe Plastic Deformation Techniques*. IntechOpen. doi:10.5772/intechopen.68965.

thickness by 50%. The rolling process is repeated for multiple times by cutting the rolled sheet in half and stacking up to initial thickness to accumulate the large plastic strains and the alignment of sheets can be changed between each cycle (see Fig. 9(a)). There are a number of parameters starting from material type (similar or dissimilar sheet metals and the reinforcement), surface properties (surface roughness, presence of moisture, contaminants, oxides, lubricants, etc.) and rolling conditions (percentage reduction, rolling speed, rolling temperature, number of layers, etc.) that affect the plastic deformation in ARB process (Tsuiji *et al.*, 2003; Ghalehbandi *et al.*, 2019). While available literature reports significant grain refinement to less than few microns in materials such as steel, aluminum alloys, copper, and nickel, edge cracks and inhomogeneous plastic deformation are also widely reported. The shear component is further enhanced by employing rolls of different diameter and rolling speed as in the case of asymmetric

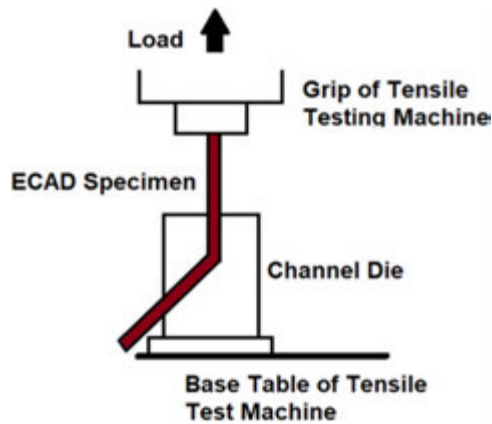


Fig. 5 Schematic of equal channel angular drawing (ECAD) process proposed by Chakkingal *et al.* Adapted from Ref. Chakkingal, U., Suriadi, A.B., Thomson, P.F., 1998. Microstructure development during equal channel angular drawing of Al at room temperature. *Scr. Mater* 39, 677–684.

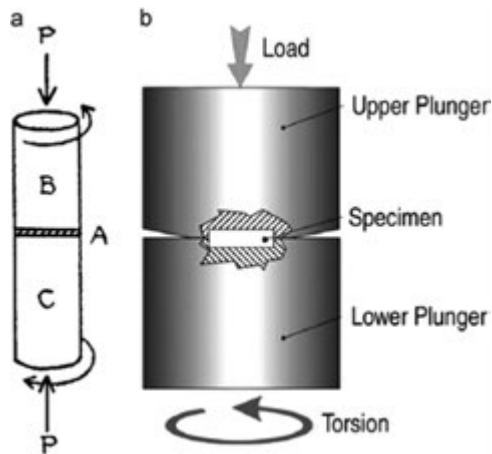


Fig. 6 Schematic of an HPT setup. Adapted from Edalati, K., Horita, Z., 2016. A review on high-pressure torsion (HPT) from 1935 to 1988. *Mater. Sci. Eng. A* 652, 325–352. doi:10.1016/j.msea.2015.11.074.

rolling as shown in Fig. 9(b) which involves the simultaneous action of compression and shear. Fig. 10 illustrates the microstructure of ARB processed Al matrix composites reinforced with graphene oxide.

Repetitive Corrugated Straightening

Repetitive corrugated straightening (RCS) or constrained groove pressing (CGS) method imparts a large amount of plastic strain by repeated bending and straightening of the workpiece. While the bending step involved pressing of the sheet material using V-shaped dies as shown in Fig. 11, straightening involved pressing the corrugated sheet using flat dies. Therefore, the RCS method does not affect the overall dimension of the work piece and one of the major advantages of RCS method is that it can be easily adapted to the current industrial rolling facilities by incorporating corrugated teeth to the rollers.

Fig. 12 shows the microstructure of fine-grained Cu processed by RCS method. It highlights the high dislocations density in the Cu grains of size less than few hundred nanometers when compared to as-annealed condition (prior to RCS processing) with an average grain size of 765 μm (Huang *et al.*, 2001).

Continuous SPD Techniques

Unlike the SPD processes as discussed earlier where specific short-dimension specimens are used, latest developments focus on continuous techniques such as con-shearing, continuous severe plastic deformation, continuous repetitive corrugation and straightening etc. These continuous processes often combine the benefits of SPD and rolling methods as illustrated in Fig. 13 and are mostly applicable for sheet metal composites.

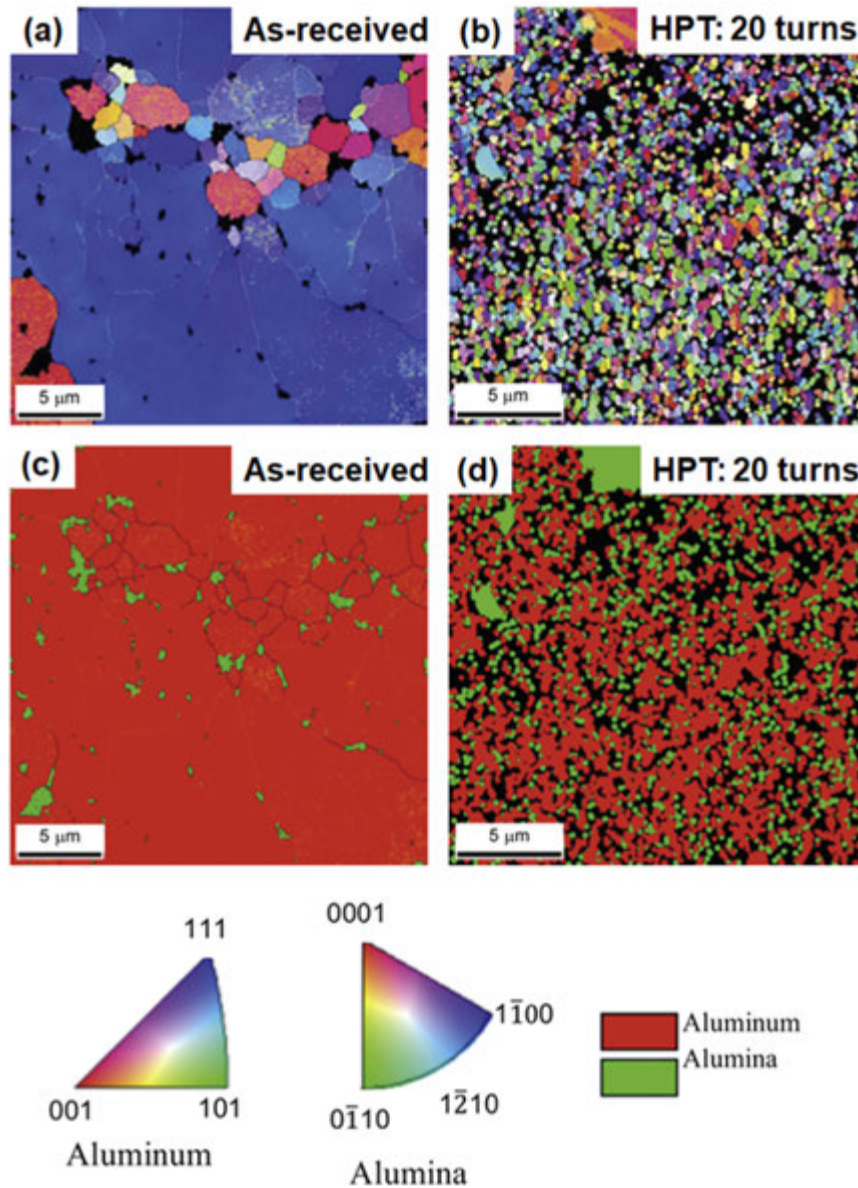


Fig. 7 Micrographs showing grain characteristics (a–b) and reinforcement distribution (c–d) in Al 7075 + 10% Al₂O₃ composite processed by high pressure torsion. Adapted from Sabbaghianrad, S., Langdon, T.G., 2016. Developing superplasticity in an aluminum matrix composite processed by high-pressure torsion. *Mater. Sci. Eng. A* 655, 36–43. doi:10.1016/j.msea.2015.12.078.

Microstructural Evolution During Severe Plastic Deformation

Severe plastic deformation-induced grain refinement has been extensively studied for fabricating ultra-fine-grained (UFG) metals. In general, the grain refinement during SPD processing depends on several factors such as process parameters including plastic strain, strain rate, strain path, temperature, and materials properties including the crystalline structure, stacking fault energy (SFE) and initial grain size (Bagherpour *et al.*, 2019). According to Tao and Lu (2009), significant grain refinement can be achieved by increasing the strain rate and reducing the temperature. They also related the strain rate ($\dot{\epsilon}$) and temperature (T) using Zener Hollomon parameter ($Z = \dot{\epsilon} \exp(-Q/RT)$, where Q is the activation energy and R is the gas constant) and showed that the critical value of Z depends on the stacking fault energy (SFE) which determines the extent of deformation by dislocation slip or twinning. While the dislocation slip is dominant in high SFE materials, twinning governs the deformation in low to medium SFE (Kawasaki and Langdon, 2015a).

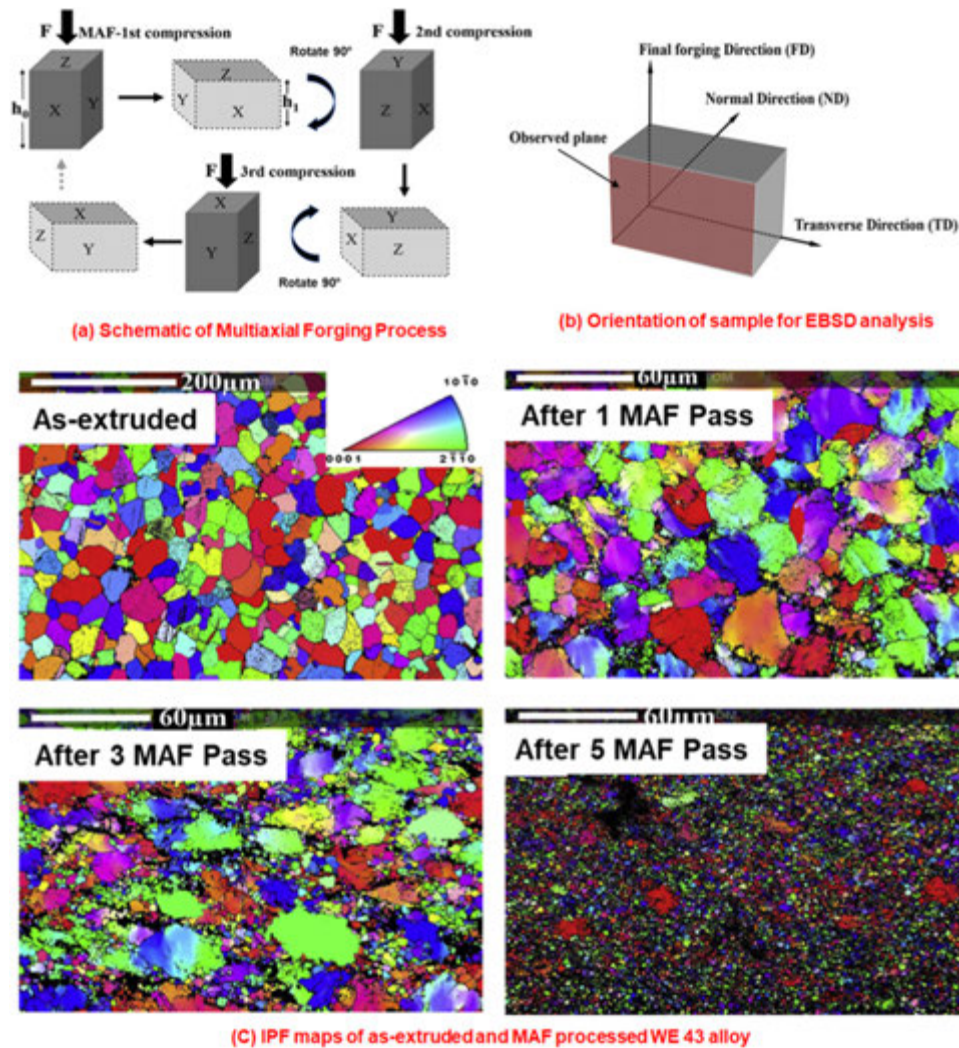


Fig. 8 Microstructural evolution during the multi-axial forging of WE43 magnesium alloy. Reproduced from Salandari-Rabori, A., Zarei-Hanzaki, A., Abedi, H.R., Lecomte, J.S., Khatami-Hamedani, H., 2018. Micro and macro texture evolution during multi-axial forging of a WE43 magnesium alloy. *J. Alloy. Compd* 739, 249–259. doi:10.1016/j.jallcom.2017.12.181.

Published literatures highlight the mechanism of dislocation dependent grain refinement mechanism in FCC structured Ni and Al with high stacking fault energy (SFE) values (in the range ~ 130 – 280 mJ/m^2) (Verlinden, 2004; Kawasaki and Langdon, 2015a; Cao *et al.*, 2018; Wang *et al.*, 2008). It consists of five stages as shown in Fig. 14. In the first stage, the dislocation cells and cell structures group together and form dislocation cell blocks which reduce in size at stage 2 due to the formation of microbands and the reorientation of early formed dislocation cells. At stage 3, the dense microbands along with the increase in misorientation angles and the continuous reduction of cell block sizes result in the formation of a large amount of lamellar sub-grains enclosed by lamellar boundaries which tend to align parallel to the shear strain direction. The increasing strain then sharpens the inter-connecting boundaries to result in a finer lamellar structure in Stage 4 and the grain refinement reaches a steady state with mostly equiaxed grains at Stage 5.

In case of low SFE materials like Cu–30 wt% Zn alloy (with a very low SFE of ~ 7 mJ/m^2), the deformation process is primarily governed by the formation of nano-twins (Cao *et al.*, 2018; Zaynullina *et al.*, 2019; Zhang *et al.*, 2011). The mechanism is schematically illustrated in Fig. 15. Here, the coherent twin boundaries that are effective in restricting the dislocation slips are transformed into grain boundaries. Therefore, the steady state grain size of SPD processed low SFE materials are comparable to that the twin boundary spacing. However, in some cases, as very thin nano-twins are formed at the early stage of deformation which upon interaction with the primary coherent twin boundaries result in de-twinning which then leads to a slightly larger grain size (Fig. 16). Since, the mode and extent of deformation are also affected by the initial grain size, the grain refinement and grain growth mechanisms require a dynamic balance in SPD processing to achieve preferred grain size and grain orientation.

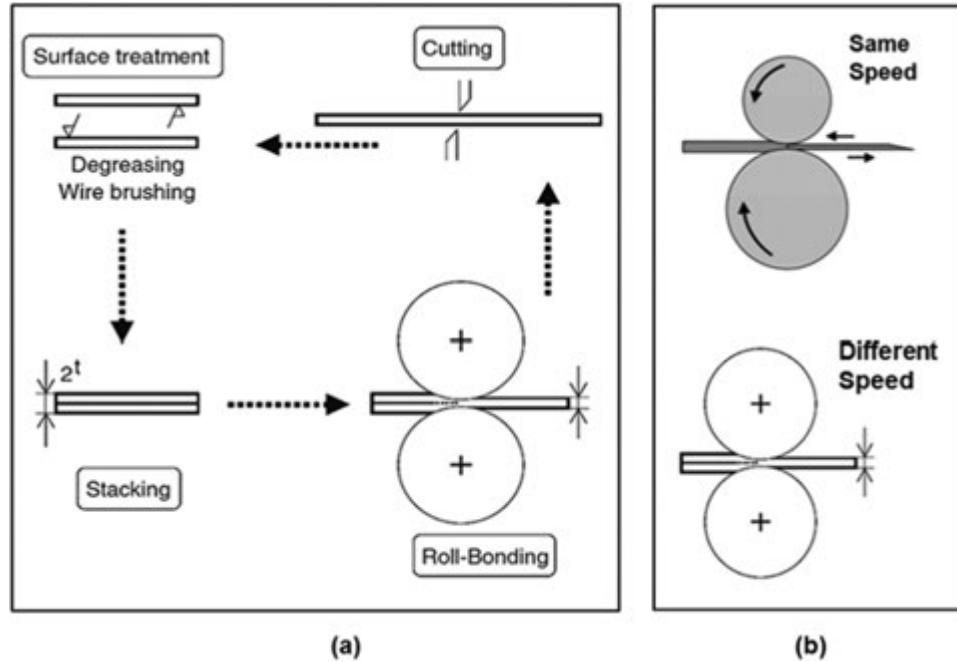


Fig. 9 Schematic of (i) accumulated roll bonding processes and (ii) asymmetric rolling setup. Adapted from Ref. Verlinden, B., 2004. Severe plastic deformation of metals. *Metal. -J. Metall* 11 (3), 165–182.

Mechanical Properties of SPD Processed Metal Matrix Composites

Mechanical property enhancement has been the primary driving force behind the development of advanced materials processing methods. Since SPD methods impose a large strain when compared to the conventional materials processing and shaping methods, they can produce bulk nanostructured materials that offer a better combination of mechanical properties including strength and ductility as shown in [Table 1](#).

In general, the mechanical properties of SPD processed materials are primarily affected by the microstructural characteristics (grain size, precipitates, phase transformation, crystal structure, etc.) that are affected by the intrinsic properties of the material and the processing/deformation conditions ([Dieter and Bacon, 1988](#); [Wagner et al., 2017](#)). During SPD processing, the high strain imposed on the material leads to high dislocation density and grain refinement ([Dieter and Bacon, 1988](#); [Callister and Rethwisch, 2007](#)). Therefore, strain hardening and grain boundary strengthening are the two major strengthening mechanisms operative in SPD processed materials. While the strengthening contribution ($\Delta\sigma_d$) resulting from dislocation accumulation or strain hardening is given by the Bailey–Hirsch relationship, Hall-Petch equation describes the strength increase due to strengthening by grain/twin boundaries ($\Delta\sigma_{HP}$) ([Cao et al., 2018](#); [Balogh et al., 2010](#)).

$$\Delta\sigma_d = M\alpha_T bG\sqrt{\rho_t} \quad (4)$$

$$\Delta\sigma_{HP} = k_{GB}D_B^{-1/2} + k_{TB}\lambda_{TB}^{-1/2} \quad (5)$$

where M – Mean orientation factor (dimensionless)

α_T – dimensionless constant between 0.3 and 0.5 depending on temperature.

b – Burgers vector in nm.

G – shear modulus in GPa.

ρ_t – Total dislocation density in m^{-2} .

k_{GB} – Hall Petch coefficient for GB strengthening in MPa/m.

D_B – Average grain size in nm.

k_{TB} – Hall Petch coefficient for twin boundary strengthening in MPa/m.

λ_{TB} – Average twin boundary spacing in nm.

In this regard, the factors including SFE and crystal structure of the materials play an important role ([An et al., 2009](#); [Qu et al., 2009](#)). For example, twin boundary (TB) strengthening is dominant in low SFE materials as the deformation is mostly twinning controlled and the TB spacing is significantly small compared to the GB spacing. Further, it is also widely reported that the change in dominant deformation mechanism from dislocation slip to twinning with decreasing SFE improves the strength properties.

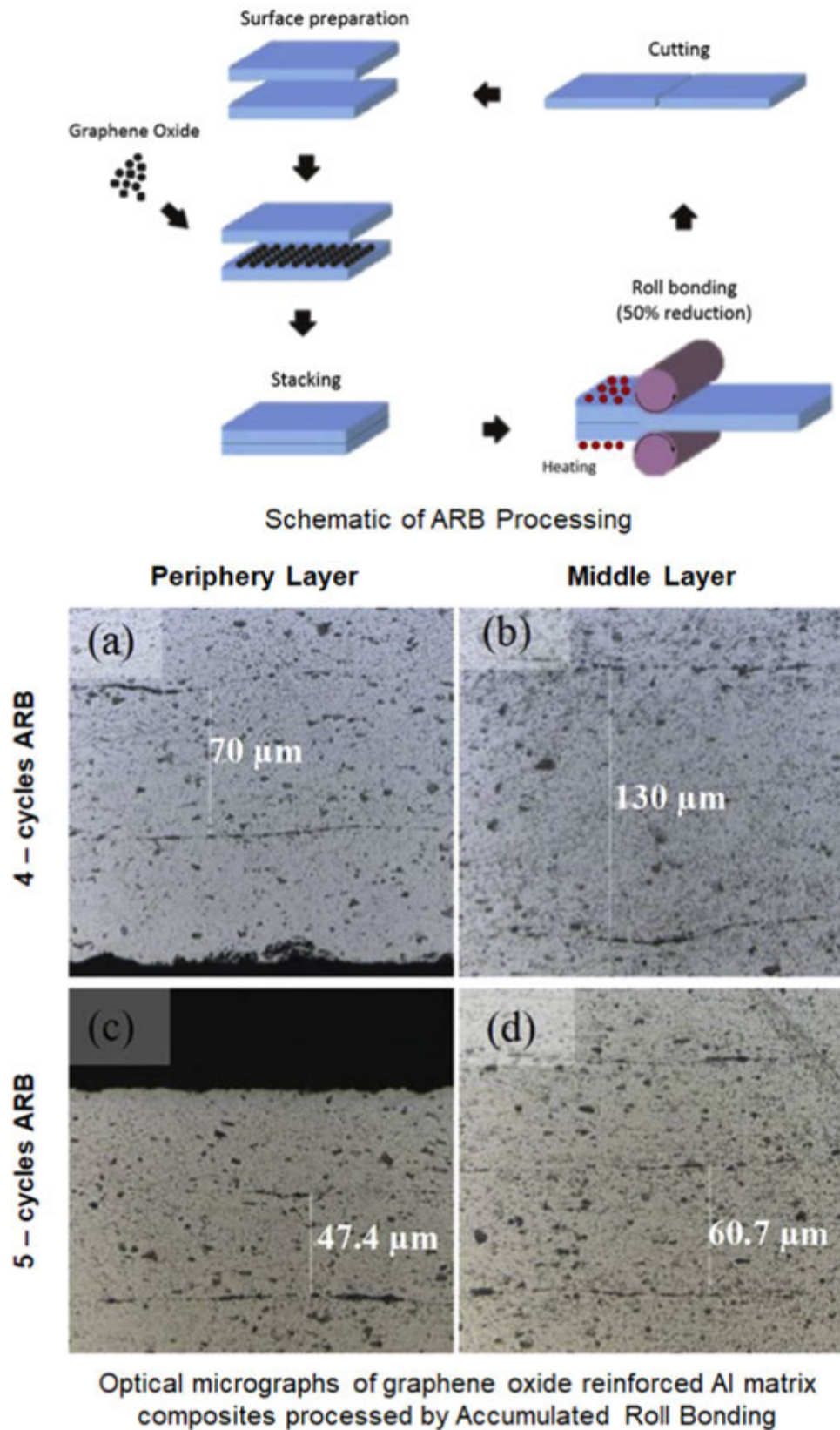


Fig. 10 Microstructure in graphene oxide reinforced Al composites processed by ARB. Adapted from Ferreira, F., Ferreira, I., Camacho, E., *et al.*, 2019. Graphene oxide-reinforced aluminium-matrix nanostructured composites fabricated by accumulative roll bonding. *Compos. Part B Eng* 164, 265–271. doi:10.1016/j.compositesb.2018.11.075.

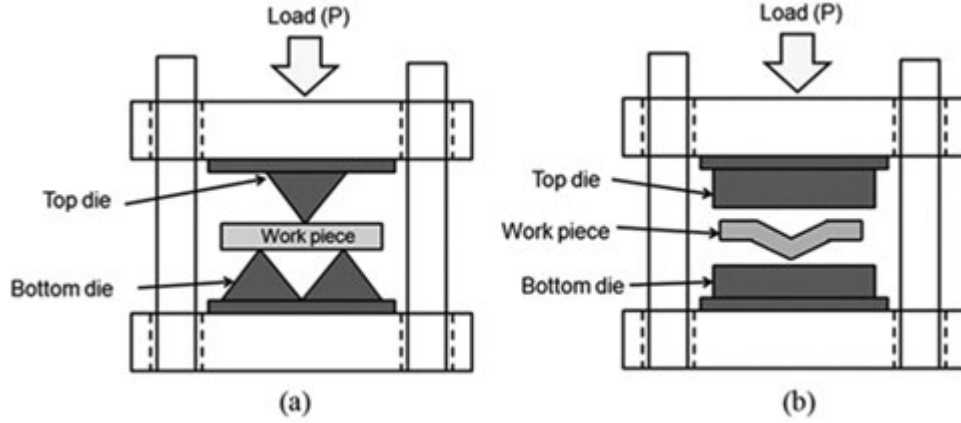


Fig. 11 Schematic of repetitive corrugation and straightening (RCS) process. Adapted from Sunil, B.R., 2015. Repetitive corrugation and straightening of sheet metals. *Mater. Manuf. Process* 30, 1262–1271. doi:10.1080/10426914.2014.973600. Huang, J.Y., Zhu, Y.T., Jiang, H., Lowe, T.C., 2001. Microstructures and dislocation configurations in nanostructured Cu processed by repetitive corrugation and straightening. *Acta Mater* 49, 1497–1505. doi:10.1016/S1359-6454(01)00069-6.

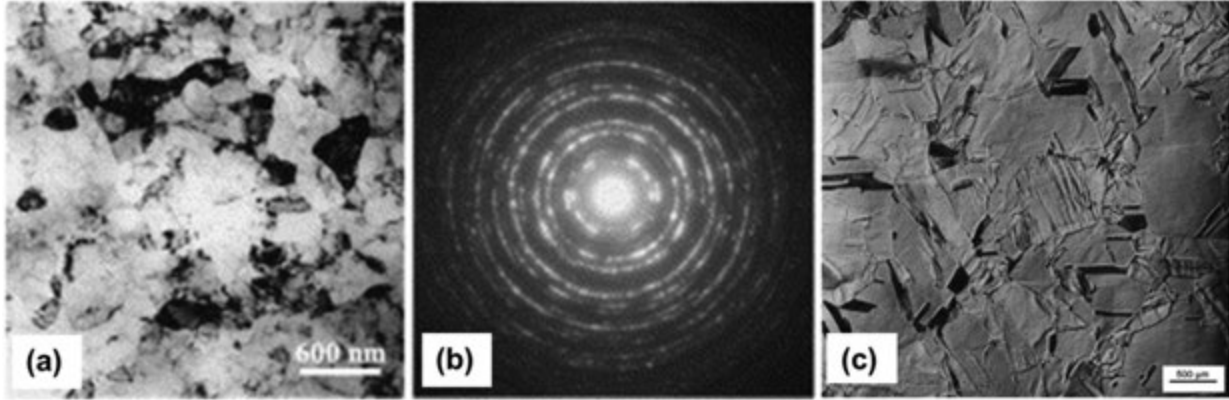


Fig. 12 (a–b) TEM micrograph and corresponding SAED pattern showing nanostructured grains in RCS processed Cu. (c) Microstructure of as-annealed Cu prior to RCS processing. Adapted from Huang, J.Y., Zhu, Y.T., Jiang, H., Lowe, T.C., 2001. Microstructures and dislocation configurations in nanostructured Cu processed by repetitive corrugation and straightening. *Acta Mater* 49, 1497–1505. doi:10.1016/S1359-6454(01)00069-6.

With respect to crystal structure, because of the larger critical resolved shear stress value, BCC metals tend to have larger Hall Petch coefficients and their GBs are relatively more effective in controlling the dislocation slips than the HCP and FCC metals.

Similarly, the interplay between dislocations and precipitates also offer strengthening effects. While the incoherent precipitates improve the strength by Orowan bypassing mechanism, the coherent and semi-coherent precipitates offer (1) coherency strengthening ($\Delta\sigma_{cs}$), (2) modulus mismatch strengthening ($\Delta\sigma_{ms}$) and (3) order strengthening ($\Delta\sigma_{os}$) (Ma *et al.*, 2014; Fribourg *et al.*, 2011). Therefore, for precipitation strengthening based on the dislocation shearing mechanism, the sum of ($\Delta\sigma_{cs} + \Delta\sigma_{ms}$ or $\Delta\sigma_{os}$) will be significant.

$$\Delta\sigma_{orowan} = M \frac{0.4 G b \ln\left(\frac{2\bar{r}}{b}\right)}{\pi\sqrt{1-v} \lambda_p} \quad (6)$$

$$\Delta\sigma_{cs} = M \alpha_e (G \epsilon_c)^{\frac{1}{2}} \left(\frac{r f}{0.5 G b} \right)^{\frac{1}{2}} \quad (7)$$

$$\Delta\sigma_{ms} = M 0.0055 (\Delta G)^{\frac{1}{2}} \left(\frac{2f}{G} \right)^{\frac{1}{2}} \left(\frac{r}{b} \right)^{\frac{3m}{2}-1} \quad (8)$$

$$\Delta\sigma_{os} = M 0.81 \frac{\gamma_{apb}}{2b} \left(\frac{3\pi f}{8} \right)^{1/2} \quad (9)$$

where $\bar{r}$ – Mean cross section radius of a precipitate in a random plane in nm

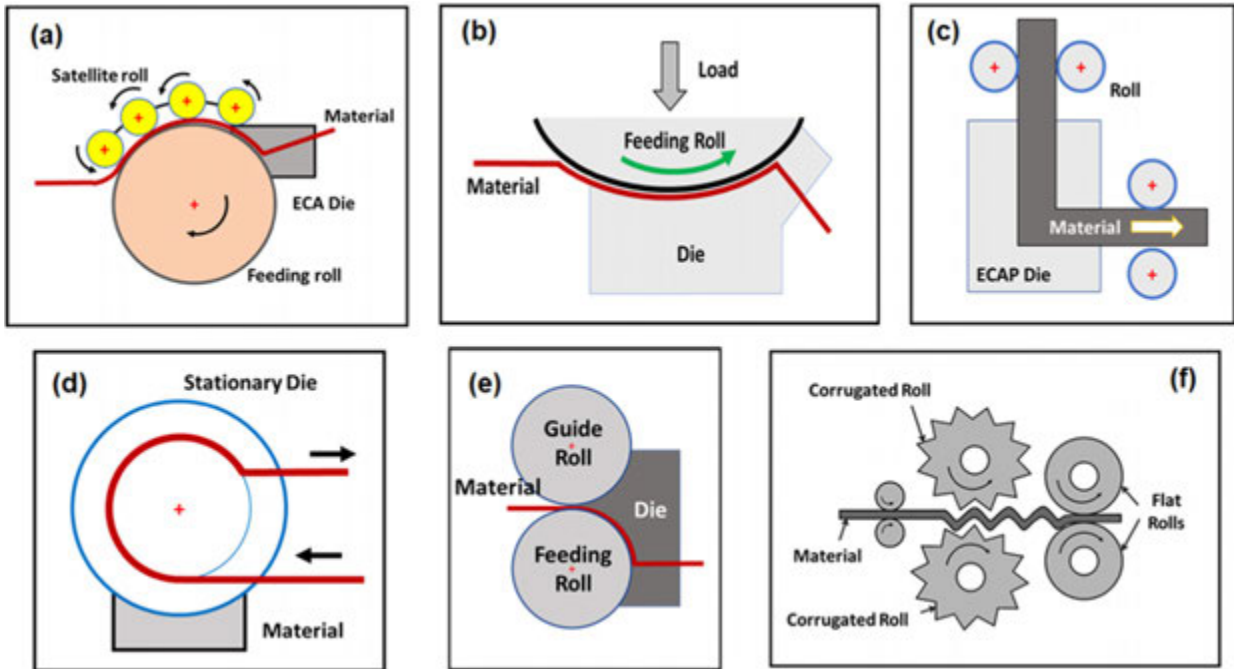


Fig. 13 Schematic of continuous SPD techniques: (a) con-shearing, (b) continuous friction angular extrusion (CFAE), (c) continuous severe plastic deformation (CSPD), (d) ECAP-conform, (e) continuous confined strip shearing (C2S2) and (f) continuous repetitive corrugations and straightening. Adapted from Ref. Faraji, G., Torabzadeh, H., 2019. An overview on the continuous severe plastic deformation methods. *Mater. Trans.* 60, 1316–1330. doi:10.2320/matertrans.MF201905.

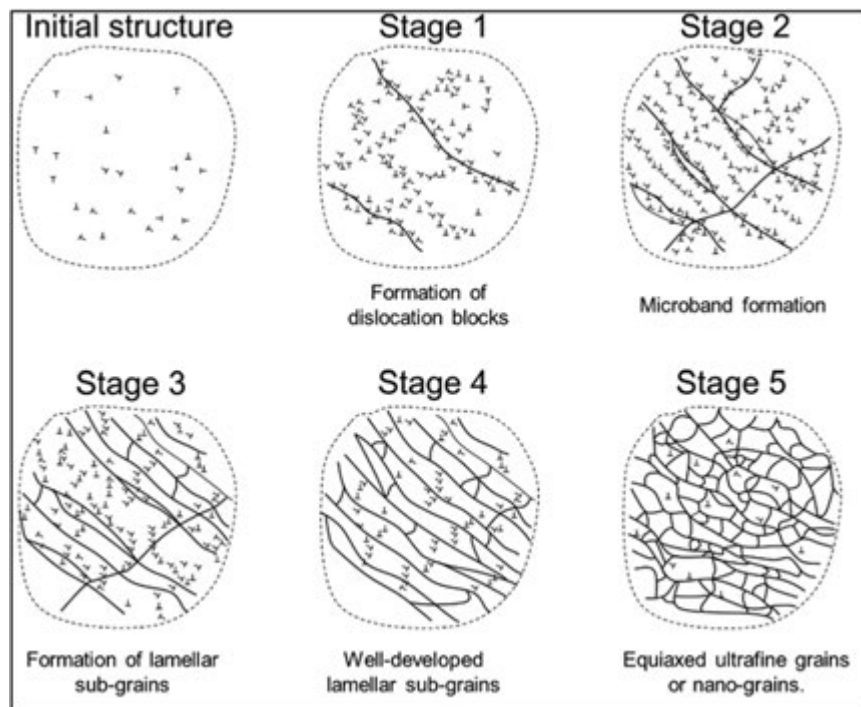


Fig. 14 Schematic illustration of grain refinement during the SPD of high SFE materials. Adapted from Cao, Y., Ni, S., Liao, X., Song, M., Zhu, Y., 2018. Structural evolutions of metallic materials processed by severe plastic deformation. *Mater. Sci. Eng. R Rep* 133, 1–59. doi:10.1016/j.mser.2018.06.001.

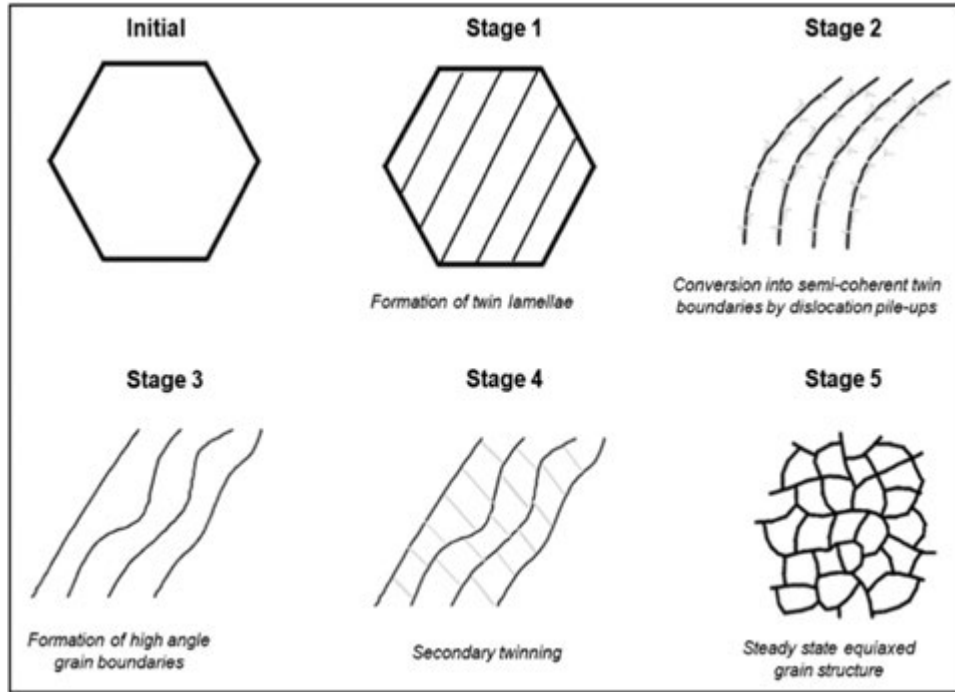


Fig. 15 Schematic illustrations of twinning induced grain refinement. Adapted from Cao, Y., Ni, S., Liao, X., Song, M., Zhu, Y., 2018. Structural evolutions of metallic materials processed by severe plastic deformation. *Mater. Sci. Eng. R Rep* 133, 1–59. doi:10.1016/j.mser.2018.06.001.

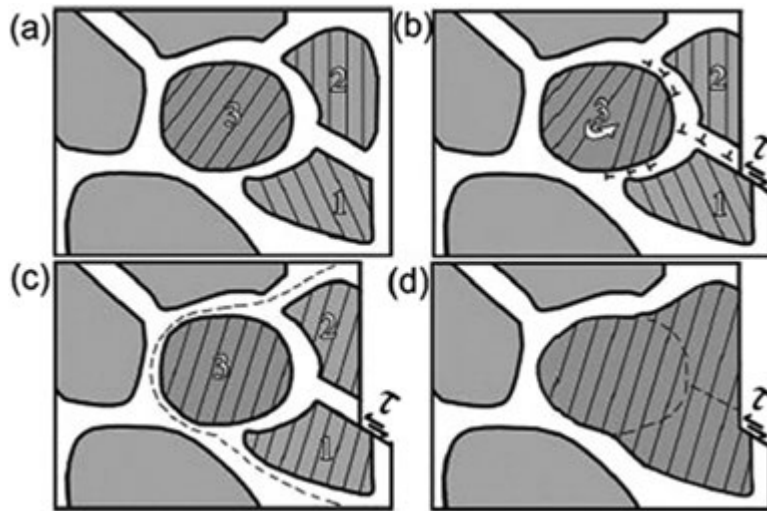


Fig. 16 Schematic of grain growth via twinning and de-twinning process: (a) formation of primary twins within nanograins, (b) accumulation of dislocations and grain boundary sliding, (c) secondary twinning leading to grain coalescence and (d) large grain formation. Adapted from Wang, Y.B., Li, B.Q., Sui, M.L., Mao, S.X., 2008. Deformation-induced grain rotation and growth in nanocrystalline Ni. *Appl. Phys. Lett.* doi:10.1063/1.2828699.

ν – Poisson ratio.

λ_p – interparticle spacing in nm.

α_e – dimensionless constant between 2 and 3.

ε_c – Constrained lattice parameter misfit (dimensionless).

r – mean radius of precipitates in nm.

f – vol% of precipitates.

m – dimensionless exponent (often, 0.85).

γ_{apb} – Boundary free energy of precipitate in J/m².

Table 1 Mechanical properties of SPD processed MMCs

Material	SPD Method	Grain Size (μm)	Yield Strength (MPa)	Tensile Strength (MPa)	Ductility (%)	Reference
Al	Starting material, extruded	—	65	—	12	Muñoz-Morris <i>et al.</i> (2006, 2005)
	ECAP- 2 Pass	—	170	—	3	
Al-25%TiAl (20 $\pm$ 25 μm)	Starting material, extruded	2.5	82	—	8	Ramu and Bauri (2009)
	ECAP-A 2 Pass	610 nm	158	—	0.6	
	ECAP-A 4 Pass	520 nm	165	—	0.6	
Al-5%SiC	Starting material	45	85	—	—	
	ECAP – 1 Pass	—	121	—	—	
	ECAP – 2 Pass	8	149	—	—	
Al-10%SiC	Starting material	45	90	—	—	Shobha <i>et al.</i> (2014)
	ECAP – 1 Pass	16	125	—	—	
Al	as-cast	—	—	130	18	
Al-2%in-situTiB ₂		—	—	140	13	
Al-4%in-situTiB ₂		—	—	165	11.5	
Al-6%in-situTiB ₂		—	—	180	11	
Al-10%in-situTiB ₂		—	—	140	10.2	
Al-12%in-situTiB ₂		—	—	135	11	
Al	ECAP – 2 Pass	—	—	150	18	
Al-2%in-situTiB ₂		—	—	160	13	
Al-4%in-situTiB ₂		—	—	200	11	Torabi <i>et al.</i> (2020)
Al-6%in-situTiB ₂		—	—	220	10	
Al-10%in-situTiB ₂		—	—	160	9	
Mg	cyclic extrusion + ECAP +	22.64	112	176	4.7	
Mg-2%HA	normal extrusion	21.23	140	233	6.4	
Mg-5%HA		16.31	195	280	5.8	Xu <i>et al.</i> (2020)
Mg-10%HA		19.70	96	256	6.2	
AZ91-5SiC (5 μm)	Starting material	150	86	192	8.2	
	90° RD-ECAP – 4 Pass	1.5	234	306	6.7	
	90° RD-ECAP –16 Pass	<0.5	225	285	8.3	Abbas and Huang (2020)
AZ91	Starting material	—	85.406	145.3	0.075	
AZ91-0.3WS ₂		—	86.761	192.7	0.258	
AZ91-0.6WS ₂		—	76.035	178.6	0.218	
AZ91-1.0WS ₂		—	93.468	175.402	0.161	
AZ91	ECAP-1 Pass	—	80.032	153.719	0.076	Huang and Ali (2019)
AZ91-0.3WS ₂		—	86.763	157.458	0.098	
AZ91-0.6WS ₂		—	93.398	194.0	0.164	
AZ91-1.0WS ₂		—	91.125	207.846	0.205	
AZ91	ECAP – 2 Pass	—	84.936	162.0	0.092	
AZ91-0.3WS ₂		—	103.654	198.6	0.143	Huang and Ali (2019)
AZ91-0.6WS ₂		—	111.380	214.7	0.156	
AZ91-1.0WS ₂		—	104.317	210.3	0.144	
AZ61	ECAP – 1 Pass	17.9	143.9	354.53	0.202	
	ECAP – 2 Pass	17.3	135.2	376.95	0.27	
AZ61-2SiC	ECAP – 1 Pass	18	137.3	358.5	0.28	
	ECAP – 2 Pass	16.8	135	352.5	0.23	
AZ61-5SiC	ECAP – 1 Pass	13.9	112.2	278.4	0.13	
	ECAP – 2 Pass	13.5	128.1	281.2	0.16	

Table 1 Continued

Material	SPD Method	Grain Size (μm)	Yield Strength (MPa)	Tensile Strength (MPa)	Ductility (%)	Reference
Al sheet (100 mm $\times$ 40 mm $\times$ 2 mm)	ECAP – 8 Pass	15.8	103.8	205.5	0.05	Tiwari <i>et al.</i> (2020)
	Starting material	72	49	107	43	
	ARB – 2 Pass	45	100	218	24	
	ARB – 4 Pass	30	106	218	15	
	ARB – 6 Pass	18	112	215	19	
	ARB – 8 Pass	8	120	220	20	
	ARB – 10 Pass	5.7	122	225	26	
Al-0.05%graphene	ARB – 10 Pass	5.1	140	250	19	Dehsorkhi <i>et al.</i> (2011)
Al-0.1%graphene	ARB – 10 Pass	4.3	152	260	19	
Al-0.15%graphene	ARB – 10 Pass	4.1	128	225	16	
Al-0.2%graphene	ARB – 10 Pass	3.9	120	210	13	
AA1050-Zn alloy sheets (73 wt% Al-27 wt% Zn)	ARB– 1 Pass	–	225	280	6	
	ARB– 2 Pass	–	240	290	10	
	ARB– 5 Pass	–	250	300	8	
	ARB– 10 Pass	–	300	372	6	
AA1050-1SiC (5 μm)	Starting material	–	30	60	48	Alizadeh and Paydar (2010)
	ARB – 1 Pass	700 nm	120	145	8	
	ARB – 4 Pass	340 nm	145	180	10	
	ARB – 8 Pass	180 nm	175	245	18	
Cu	High pressure torsion	304 $\pm$ 6 nm	500	–	16	Korznikova <i>et al.</i> (2020)
Cu + graphene		292 $\pm$ 8 nm	250	–	4	
Mg	HPT 5 turns	–	47 (Hv)	–	–	Castro <i>et al.</i> (2019)
Mg-10%Al ₂ O ₃		–	$\sim$ 75 (Hv)	–	–	
Al-Cu-Al composite	HPT, 20 turns	20 nm	280 $\pm$ 21	420 $\pm$ 30	3.1 $\pm$ 1.1	Bazarnik <i>et al.</i> (2020)
	HPT, 50 turns		370 $\pm$ 27	460 $\pm$ 25	1.5 $\pm$ 0.6	
	HPT, 150 turns		540 $\pm$ 23	710 $\pm$ 34	1.7 $\pm$ 0.3	
	HPT, 200 turns		680 $\pm$ 22	910 $\pm$ 16	2.2 $\pm$ 0.5	

In addition, the lattice friction together with the local strain field generated due to the difference in atomic radii of alloying elements also obstruct the dislocation slip, thereby leading to solid solution strengthening ($\Delta\sigma_{ss}$) (Fleischer, 1962).

$$\Delta\sigma_{ss} = M G b \varepsilon_{ss}^{3/2} \sqrt{C} \quad (10)$$

where ε_{ss} – dimensionless parameter that accounts for the local resistance to dislocation propagation, C – concentration of solute atoms in wt%.

Therefore, the overall yield strength can be determined by the sum of strengthening contributions from various mechanisms as shown below (Ma *et al.*, 2014):

$$\sigma_y = \sigma_o + \Delta\sigma_d + \Delta\sigma_{HP} + \Delta\sigma_{ss} + \Delta\sigma_p \quad (11)$$

where σ_o refers to the lattice friction stress

While most SPD processed materials possess very high strength, only a few with a high density of intragranular solute clusters and/or nano-sized second-phase particles, or a large number of coherent TBs that are effective in blocking the dislocations exhibit outstanding combination of strength and ductility (Table 1). Here the unique micro/nanostructure offers additional strain hardening capability to delay the localized plastic strain instability. Similar ductility improvements are also reported for gradient nanostructure (nanostructured surface layers and coarse-grained core) and hetero-structured (agglomerated coarse grains embedded within nanostructured matrix) materials (Wu and Zhu, 2017; Ma and Zhu, 2017; Fang *et al.*, 2011, 2014). The ductility of SPD processed materials is also improved by increasing the strain rate sensitivity. However, this approach is less effective as the strain rate sensitivity of most materials is relatively small at room temperature (Ovid'ko *et al.*, 2018).

In some cases, severe plastic deformation leads to super plasticity which refers to the capability of a material to undergo very large plastic deformation (Langdon, 1982). While the fundamental requirement for super plasticity in conventional polycrystalline materials involves grain boundary sliding that requires a fine grain size less than 10 μm and a homologous temperature above 0.5 T_m at strain rates between 10⁻³/s to 10⁻⁴/s, a classical dislocation glide mechanism will be active in metal matrix composites

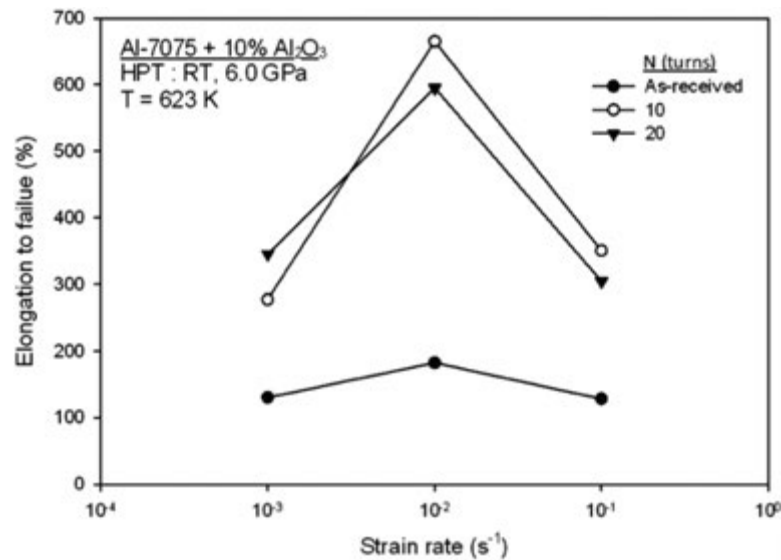


Fig. 17 Elongation to failure plotted against strain rate for the MMC in the as-received condition and after processing by HPT through 10 and 20 turns. Adapted from Sabbaghianrad, S., Langdon, T.G., 2016. Developing superplasticity in an aluminum matrix composite processed by high-pressure torsion. *Mater. Sci. Eng. A* 655, 36–43. doi:10.1016/j.msea.2015.12.078.

and powder metallurgy processed materials at low temperatures ($<0.5T_m$) and high strain rates ($>10^{-2}/s$) (Kawasaki and Langdon, 2015a,b). An example of strain induced super plasticity in metal matrix composites is illustrated in Fig. 17.

Concluding Remarks and Recommendations

Published studies demonstrate the feasibility of lab scale SPD methods such as ECAP, HPT, MAF etc. to produce ultrafine grained materials. While the downscaling of SPD processes provides an opportunity to produce UFG wires and fibers, the upscaling is not evident although interesting adaptations such as asymmetric rolling, corrugation and straightening, con-shearing, continuous confined strip shearing, ECAP-conform etc. are being developed for the continuous production of fine grained materials. Therefore, it is now reasonable to anticipate the extensive application of UFG metal matrix composites. UFG materials find significant potential for applications under extreme conditions in aircraft systems, oil and gas industry, energy, high-performance sports, bio-medical, etc. One of the established examples include ECAP processing of Al and Cu sputtering targets in the fabrication of memory components for micro electro-mechanical systems (MEMS).

SPD processing leads to a significant increase in dislocation density which results in a unique micro/nanostructured architecture. In this regard, stacking fault energy plays a critical role. While the grain refinement in high SFE materials occurs by dislocation activities, the complex interplay between the dislocation slips and the deformation twinning or twin boundaries is responsible for the grain refinement in low SFE materials. Although the grain refinement resulting from SPD processing is often stable, grain coarsening in some cases results in bimodal grain size distribution. With respect to mechanical properties, mechanisms such as dislocation strengthening, grain boundary strengthening, precipitate and solid solution strengthening improve the strengths of SPD processed materials. Similarly, the unique microstructure resulting from SPD processing offers additional strain hardening capability and delays the localized plastic strain instability for moderate improvements in ductility. With adequate thermal stability, SPD processing also opens up the possibility for high strain rate and/or low temperature super plasticity.

While the improvement in strength properties of SPD processed materials have been investigated extensively, recent studies focus on the modification of SFE and the development of gradient nanostructure (nanostructured surface layers and coarse-grained core) and hetero-structure (agglomerated coarse grains embedded within nanostructured matrix) for improved ductility.

References

- Abbas, A., Huang, S.J., 2020. Investigation of severe plastic deformation effects on microstructure and mechanical properties of WS₂/AZ91 magnesium metal matrix composites. *Mater. Sci. Eng. A* 780, 139211. doi:10.1016/j.msea.2020.139211.
- Alizadeh, M., Paydar, M.H., 2010. Fabrication of nanostructure Al/SiCP composite by accumulative roll-bonding (ARB) process. *J. Alloy. Compd* 492, 231–235. doi:10.1016/j.jallcom.2009.12.026.
- An, X., Lin, Q., Qu, S., et al., 2009. Influence of stacking-fault energy on the accommodation of severe shear strain in Cu-Al alloys during equal-channel angular pressing. *J. Mater. Res* 24, 3636–3646. doi:10.1557/jmr.2009.0426.

- Bagherpour, E., Pardis, N., Reihanian, M., Ebrahimi, R., 2019. An overview on severe plastic deformation: Research status, techniques classification, microstructure evolution, and applications. *Int. J. Adv. Manuf. Technol.* 100, 1647–1694. doi:10.1007/s00170-018-2652-z.
- Balogh, L., Figueiredo, R.B., Ungár, T., Langdon, T.G., 2010. The contributions of grain size, dislocation density and twinning to the strength of a magnesium alloy processed by ECAP. *Mater. Sci. Eng. A* 528, 533–538. doi:10.1016/j.msea.2010.09.048.
- Bazarnik, P., Bartkowska, A., Romelczyk-Baishya, B., *et al.*, 2020. Superior strength of tri-layered Al–Cu–Al nano-composites processed by high-pressure torsion. *J. Alloy. Compd* 846, 156380. doi:10.1016/j.jallcom.2020.156380.
- Callister Jr., W.D., Rethwisch, D.G., 2007. *Materials Science and Engineering: An Introduction*. Wiley. doi:10.1016/0025-5416(87)90343-0.
- Cao, Y., Ni, S., Liao, X., Song, M., Zhu, Y., 2018. Structural evolutions of metallic materials processed by severe plastic deformation. *Mater. Sci. Eng. R Rep* 133, 1–59. doi:10.1016/j.mser.2018.06.001.
- Castro, M.M., Pereira, P.H.R., Isaac, A., Figueiredo, R.B., Langdon, T.G., 2019. Development of a magnesium-alumina composite through cold consolidation of machining chips by high-pressure torsion. *J. Alloy. Compd* 780, 422–427. doi:10.1016/j.jallcom.2018.11.357.
- Chakkingal, U., Suriadi, A.B., Thomson, P.F., 1998. Microstructure development during equal channel angular drawing of Al at room temperature. *Scr. Mater* 39, 677–684.
- Verlinden, B., 2004. Severe plastic deformation of metals. *Metal. -J. Metall* 11 (3), 165–182.
- Dehsorkhi, R.N., Qods, F., Tajally, M., 2011. Investigation on microstructure and mechanical properties of Al–Zn composite during accumulative roll bonding (ARB) process. *Mater. Sci. Eng. A* 530, 63–72. doi:10.1016/j.msea.2011.09.040.
- Dieter, G.E., Bacon, D., 1988. *Mechanical Metallurgy*: SI Metric Edition. London: McGraw-Hill Book Company.
- Fang, T.H., Tao, N.R., Lu, K., 2014. Tension-induced softening and hardening in gradient nanogained surface layer in copper. *Scr. Mater* 77, 17–20. doi:10.1016/j.scriptamat.2014.01.006.
- Fang, T.H., Li, W.L., Tao, N.R., Lu, K., 2011. Revealing extraordinary intrinsic tensile plasticity in gradient nano-grained copper. *Science* 331, 1587–1590. doi:10.1126/science.1200177.
- Fleischer, R.L., 1962. Solution hardening by tetragonal distortions: Application to irradiation hardening in F.C.C. crystals. *Acta Metall* 10, 835–842. doi:10.1016/0001-6160(62)90098-6.
- Fribourg, G., Bréchet, Y., Deschamps, A., Simar, A., 2011. Microstructure-based modelling of isotropic and kinematic strain hardening in a precipitation-hardened aluminium alloy. *Acta Mater* 59, 3621–3635. doi:10.1016/j.actamat.2011.02.035.
- Furukawa, M., Horita, Z., Nemoto, M., *et al.*, 2000. Factors influencing the development of ultrafine grained materials through severe plastic deformation. In: Mishra, R. (Ed.), *Ultrafine Grained Materials: Proceedings of a Symposium: Held During the 2000 TMS Annual Meeting in Nashville, Tennessee, March 12–16*, pp. 125–134.
- Ghalebandi, S.M., Malaki, M., Gupta, M., 2019. Accumulative roll bonding – A review. *Appl. Sci* 9, 3627.
- Huang, J.Y., Zhu, Y.T., Jiang, H., Lowe, T.C., 2001. Microstructures and dislocation configurations in nanostructured Cu processed by repetitive corrugation and straightening. *Acta Mater* 49, 1497–1505. doi:10.1016/S1359-6454(01)00069-6.
- Huang, S.J., Ali, A.N., 2019. Experimental investigations of effects of SiC contents and severe plastic deformation on the microstructure and mechanical properties of SiCp/AZ61 magnesium metal matrix composites. *J. Mater. Process. Technol* 272, 28–39. doi:10.1016/j.jmatprotec.2019.05.002.
- Iwahashi, Y., Wang, J., Horita, Z., Nemoto, M., Langdon, T.G., 1996. Principle of equal-channel angular pressing for the processing of ultra-fine grained materials. *Scr. Mater* 35, 143–146. doi:10.1016/1359-6462(96)00107-8.
- Kawasaki, M., Langdon, T.G., 2015a. Review: Achieving superplastic properties in ultrafine-grained materials at high temperatures. *J. Mater. Sci* 51, 19–32. doi:10.1007/s10853-015-9176-9.
- Kawasaki, M., Langdon, T.G., 2015b. Developing superplasticity in ultrafine-grained metals. *Acta Phys. Pol. A* 128, 470–478. doi:10.12693/APhysPolA.128.470.
- Korznikova, G., Czeppe, T., Khalikova, G., *et al.*, 2020. Microstructure and mechanical properties of Cu-graphene composites produced by two high pressure torsion procedures. *Mater. Charact* 161, 110122. doi:10.1016/j.matchar.2020.110122.
- Langdon, T.G., 1982. The mechanical properties of superplastic materials. *Metall. Trans. A* 13, 689–701. doi:10.1007/BF02642383.
- Langdon, T.G., Furukawa, M., Nemoto, M., Horita, Z., 2000. Using equal-channel angular pressing for refining grain size. *JOM* 52, 30–33. doi:10.1007/s11837-000-0128-7.
- Ma, E., Zhu, T., 2017. Towards strength–ductility synergy through the design of heterogeneous nanostructures in metals. *Mater. Today* 20, 323–331. doi:10.1016/j.mattod.2017.02.003.
- Ma, K., Wen, H., Hu, T., *et al.*, 2014. Mechanical behavior and strengthening mechanisms in ultrafine grain precipitation-strengthened aluminum alloy. *Acta Mater* 62, 141–155. doi:10.1016/j.actamat.2013.09.042.
- Minárik, P., Krajčák, T., Srba, O., *et al.*, 2017. Chapter 2 – Mechanical properties and microstructure development in ultrafine-grained materials processed by equal-channel angular pressing. In: Cabibbo, M. (Ed.), *Severe Plastic Deformation Techniques*. IntechOpen. doi:10.5772/intechopen.68965.
- Muñoz-Morris, M.A., Gutierrez-Urrutia, I., Morris, D.G., 2005. Effect of equal channel angular pressing on strength and ductility of Al–TiAl composites. *Mater. Sci. Eng. A* 396, 3–10. doi:10.1016/j.msea.2004.11.046.
- Muñoz-Morris, M.A., Calderón, N., Gutierrez-Urrutia, I., Morris, D.G., 2006. Matrix grain refinement in Al–TiAl composites by severe plastic deformation: Influence of particle size and processing route. *Mater. Sci. Eng. A* 425, 131–137. doi:10.1016/j.msea.2006.03.027.
- Ovid'ko, I.A., Valiev, R.Z., Zhu, Y.T., 2018. Review on superior strength and enhanced ductility of metallic nanomaterials. *Prog. Mater. Sci* 94, 462–540. doi:10.1016/j.pmatsci.2018.02.002.
- Qu, S., An, X.H., Yang, H.J., *et al.*, 2009. Microstructural evolution and mechanical properties of Cu–Al alloys subjected to equal channel angular pressing. *Acta Mater* 57, 1586–1601. doi:10.1016/j.actamat.2008.12.002.
- Ramu, G., Bauri, R., 2009. Effect of equal channel angular pressing (ECAP) on microstructure and properties of Al–SiCp composites. *Mater. Des* 30, 3554–3559. doi:10.1016/j.matdes.2009.03.001.
- Sanusi, K.O., Makinde, O.D., Oliver, G.J., 2012. Equal channel angular pressing technique for the formation of ultra-fine grained structures. *S. Afr. J. Sci* 108, Article 212. doi:10.4102/sajs.v108i9/10.212.
- Segal, V.M., 1974. Methods of stress-strain analysis in metal forming (Ph.D. Thesis). Minsk, Russia: Physical Technical Institute Academy of Sciences of Buelorussia.
- Segal, V.M., 1999. Equal channel angular extrusion: from macromechanics to structure formation. *Mater. Sci. Eng. A* 271, 322–333. doi:10.1016/s0921-5093(99)00248-8.
- Segal, V., Goforth R.E., Hartwig K.T., 1995. *Apparatus and Method for Deformation Processing of Metals, Ceramics, Plastics and Other Materials*.
- Semiátin, S.L., DeLo, D.P., 1999. Equal channel angular extrusion of difficult-to-work alloys. *Mater. Des* 21 (4).
- Shobha, R., Suresh, K.R., Niranjana, H.B., 2014. Mechanical and microstructural evaluation of insitu aluminium titanium boride composite processed by severe plastic deformation. *Procedia Mater. Sci* 5, 281–288. doi:10.1016/j.mspro.2014.07.268.
- Tao, N.R., Lu, K., 2009. Nanoscale structural refinement via deformation twinning in face-centered cubic metals. *Scr. Mater* 60, 1039–1043. doi:10.1016/j.scriptamat.2009.02.008.
- Tiwari, J.K., Mandal, A., Rudra, A., *et al.*, 2020. Influence of graphene content on the mechanical properties of severely deformed graphene/aluminum composite. *Mater. Chem. Phys* 248, 122939. doi:10.1016/j.matchemphys.2020.122939.
- Torabi, H., Hoseini, M., Sadikhah, M., Faraji, G., Masoumi, A., 2020. Microstructure, mechanical properties and bio-corrosion properties of Mg–HA bionanocomposites fabricated by a novel severe plastic deformation process. *Ceram. Int* 46, 2836–2844. doi:10.1016/j.ceramint.2019.09.276.
- Tsuji, N., Saito, Y., Utsunomiya, H., Tanigawa, S., 1999. Ultra-fine grained bulk steel produced by accumulative roll-bonding (ARB) process. *Scr. Mater* 40, 795–800. doi:10.1016/S1359-6462(99)00015-9.

- Tsuji, N., Saito, Y., Lee, S.H., Minamino, Y., 2003. ARB (accumulative roll-bonding) and other new techniques to produce bulk ultrafine grained materials. *Adv. Eng. Mater* 5, 338–344. doi:10.1002/adem.200310077.
- Valiev, R.Z., Islamgaliev, R.K., Alexandrov, I.V., 2000. Bulk nanostructured materials from severe plastic deformation. *Prog. Mater. Sci* 45, 103–189. doi:10.1016/S0079-6425(99)00007-9.
- Valiev, R.Z., Estrin, Y., Horita, Z., *et al.*, 2006. Producing bulk ultrafine-grained materials by severe plastic deformation. *JOM*. doi:10.1007/s11837-006-0213-7.
- Wagner, S., Härtel, M., Frint, P., Wagner, M.F.X., 2017. Influence of ECAP temperature on the formability of a particle reinforced 2017 aluminum alloy. *IOP Conf. Ser. Mater. Sci. Eng* 181, 012039. doi:10.1088/1757-899X/181/1/012039.
- Wang, Y.B., Li, B.Q., Sui, M.L., Mao, S.X., 2008. Deformation-induced grain rotation and growth in nanocrystalline Ni. *Appl. Phys. Lett* 92, 011903. doi:10.1063/1.2828699.
- Wu, X., Zhu, Y., 2017. Heterogeneous materials: A new class of materials with unprecedented mechanical properties. *Mater. Res. Lett* 5, 527–532. doi:10.1080/21663831.2017.1343208.
- Xu, Q., Ma, A., Saleh, B., *et al.*, 2020. Enhancement of strength and ductility of SiCp/AZ91 composites by RD-ECAP processing. *Mater. Sci. Eng. A* 771, 138579. doi:10.1016/j.msea.2019.138579.
- Zaynullina, L.I., Alexandrov, I.V., Wei, W., 2019. Microstructure and mechanical properties of nanostructured Cu-Zn alloys by ECAP and rolling. *IOP Conf. Ser. Mater. Sci. Eng* 672, 12067. doi:10.1088/1757-899X/672/1/012067.
- Zhang, Z.J., Duan, Q.Q., An, X.H., *et al.*, 2011. Microstructure and mechanical properties of Cu and Cu-Zn alloys produced by equal channel angular pressing. *Mater. Sci. Eng. A* 528, 4259–4267. doi:10.1016/j.msea.2010.12.080.

Friction Stir Processing of Metal Matrix Composites

VK Bupesh Raja, Sathyabama Institute of Science and Technology, Chennai, India
Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction to Friction Stir Processing (FSP)

Friction stir processing (FSP) is a variant of the friction stir welding (FSW) process wherein a rotating non-consumable FSW tool is used to join the abutting metallic plates. The FSP is a solid-state material processing technique that is used to engineer the surface of the material using a rotating FSP tool. The FSP produces refined microstructure and thus enhances the mechanical properties, tribological properties, corrosion properties, fatigue resistance, etc., and eliminates defects without affecting the properties of the underlying bulk material. In FSP the non-consumable rotating tool having a profiled pin and a relatively large diameter shoulder is plunged into the surface of the work material and traversed across the surface of the material. Large surfaces are processed by rastering the transverse of the tool path. The material gets thermomechanically processed due to frictional heat between the FSP tool and surface of the material and flow of the plasticized material around the tool and consolidation by the ironing action of the shoulder of the tool. The schematic of the friction stir processing technique is shown in [Fig. 1](#). ([Sharma et al., 2015](#)).

Fabrication of Surface Composites (SCs) by FSP

The traditional techniques used for fabricating SCs involve molten metal (liquid phase) processing techniques like plasma spraying and laser melt treatment. These techniques are prone to deterioration of the properties of the composite caused by the reinforcement-matrix interfacial reaction. ([Pantelis et al., 1995](#); [Meng et al., 2013](#); [Sharma et al., 2015](#)).

In the initial stages of FSP, the SCs were fabricated by applying volatile slurry comprising of ceramic particles above the substrate over which the FSP tool plows through forming the SC. ([Mishra et al., 2003](#)). Currently, the practice is to fill the ceramic particles in a machined groove on the substrate. ([Arora et al., 2012](#)). To improve the homogeneity in the distribution of the reinforcing particles, the particles are filled in blind holes drilled on the substrate. ([Li et al., 2013](#)). To prevent the ejection of the reinforced particles from the holes a thin cover plate is used over the drilled substrate and subjected to FSP. ([Lim et al., 2009](#); [Avettand-Fènoël et al., 2014](#)). In some other approaches functionally graded SC was fabricated on AA6082-T6 using a consumable tool filled with reinforcement particles. ([Gandra et al., 2013, 2014](#); [Miranda et al., 2013](#)).

In another approach, a direct friction stir processing (DFSP) was applied on the AZ31 matrix. Here a hollow probe less tool filled with reinforcement particles was used to fabricate the SC. Here the particles flowed out of the hollow tool and get pressed into the substrate by the rotating transversing tool. ([Huang et al., 2014](#)).

Classification of Friction Stir Processed Surface Composites

The surface composites fabricated through friction stir processing are broadly classified into six types as given below: ([Sharma et al., 2015](#)).

- (1) Surface Nano-Composites.
- (2) Surface Micro-Composites.
- (3) Surface hybrid composites.
- (4) Surface-Powder metallurgy in-situ composites/Intermetallic Powder Composite.
- (5) Surface Metal Powder Composites/Surface Composites SCs.
- (6) Surface Bulk Composites.

Surface Nano-Composites

The addition of ZrO_2 of an average size of 40 nm to the surface of AZ31 alloy through FSP using an H13 hot work tool steel, pinless tool rotating at 1250 rpm and traversing at 20 mm/min and a tool tilt of 2.5 degrees was attempted. The exposure to more FSP passes resulted in the formation of ultra-fine grains which was attributed to the Zener-pinning effect. The ZrO_2 nanoparticles prevent the growth of the high-angle grains at high temperatures, by pinning the grain boundaries, thus increasing the hardness and tensile strength of the FSPed surface composite. Further, these fine grains offer resistance to the motion of dislocations and thus enhance the hardness and tensile strength of the surface composite ([Navazani and Dehghani, 2016](#)). This behavior conforms with the Hall-Petch type of equation. ([Chang et al., 2004](#)).

$$H_v = 40 + 72d^{-1/2} \quad (1)$$

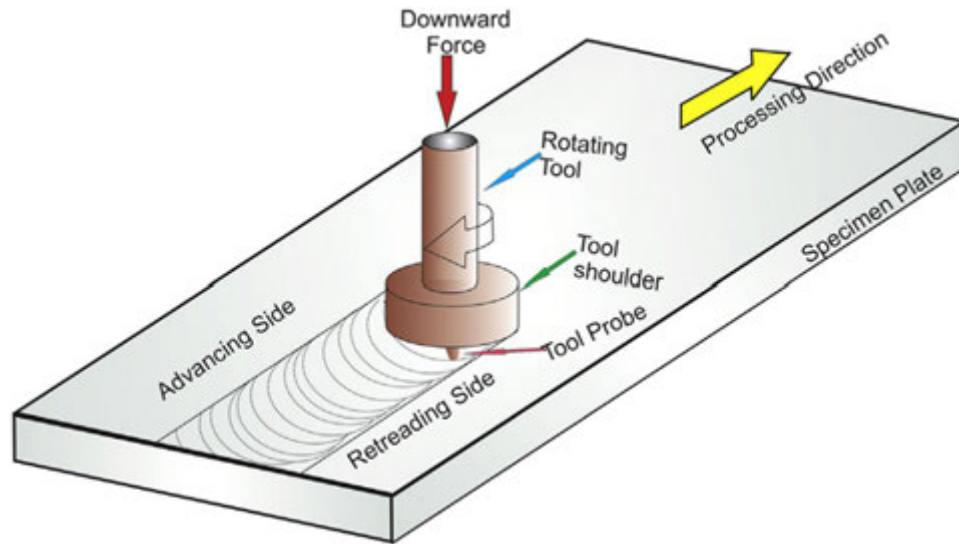


Fig. 1 Schematic of friction stir processing technique. Reproduced from Sharma, V., Prakash, U., Kumar, B.V.M., 2015. Surface composites by friction stir processing: A review. *Journal of Materials Processing Technology* 224, 117–134. Available at: <https://doi.org/10.1016/j.jmatprotec.2015.04.019>.

Where H_v is the microhardness readings in the various zones of FSPed surface composite and d is the average grain size of the surface composite.

Sheets of aluminum-magnesium alloy AA5052 FSPed with TiO_2 nanoparticles of a mean diameter of around 20 nm using a H13 tool yielded good tensile strength and hardness. The high heat peaks in the advancing side due to severe plastic straining and deformation influenced the microstructure and mechanical properties of the surface nanocomposite. The higher ω/v ratio where ω is rotational speed and v is the traverse velocity; ensured uniform distribution of the nanoparticles in the AA5052 matrix ensuring the pinning of the grain boundaries and the associated formation of ultrafine grains and enhanced solid-state chemical reactions. Further, the grain size in the stir zone (SZ) was mainly influenced by the rotational speed, than the traverse velocity. (Khodabakhshi *et al.*, 2017).

The AZ61A billets incorporated with 5–10 vol% of SiO_2 nanoparticles of average diameter around 20 nm were processed through FSP using fixed pin FSP tool with a 2° tilt angle operating at a rotational speed of 800 rpm and advancing speed of 45 mm/min. With four passes it yielded a good distribution of the nano SiO_2 particles which react with the Mg in the matrix and forms Mg_2Si and MgO phase of 5–200 nm size. The nanocomposite exhibited a high strain rate superplasticity (HSR SP) of over 400% due to the uniform distribution of SiO_2 at elevated temperature occurring during the multiple passes of FSP (Lee *et al.*, 2006). The surface nanocomposite $\text{SiO}_2/\text{AZ31}$ produced through FSP exhibited grain refinement-associated formation of ultrafine grains and enhanced hardness. The nano SiO_2 particles of around 20 nm were FSPed at a rotating speed of 1200 rpm and a 50 mm/min travel speed. (Jiang *et al.*, 2013). The fine grain formation was attributed to the smaller particle interspacing (L). This is represented in Eq. 2. (Ardell, 1985).

$$L = d/2(2\prod/3V_f)^{1/2} \quad (2)$$

where

d is average particle diameter and V_f is particle volume fraction.

Hence according to Eq. 2, the ductility of the composite shall reduce as the V_f increases. Also, the L decreases with a reduction in d , and hence FSP improves the particle interspacing and breaking the reinforcement particles to a smaller size.

The underwater submerged FSP of AA5083/ Al_2O_3 surface composite produced a good reduction in grain size and enhanced mechanical properties. The Al_2O_3 nanoparticles of 80 nm and the shorter thermal cycle in the submerged FSP coupled with multiple FSP pass yielded enhanced properties. The enhanced mechanical properties were mainly attributed to the Hall-Petch effect than the Orowan mechanism. (Ashjari *et al.*, 2015).

In AZ31/ Al_2O_3 nano surface composite, the increase in frictional heat with the increase in rotational speed of the FSP tool caused the shattering of the nanoparticles and their uniform distribution, and the associated grain refinement with every pass of the multipass FSP cycle. Here dislocation pinning effect strengthened the composite. (Azizieh *et al.*, 2011). The presence of finely dispersed alumina (Al_2O_3) caused due to FSP limited the grain growth and resulted in ultrafine grain size as governed by Zener limiting grain size (d_z). (Martin *et al.*, 1997).

$$\text{Zener limiting grain size } d_z = 4r/3V_f \quad (3)$$

Where

r is the radius of the reinforcement particles and

V_f is the volume fraction of clustered reinforcement particles

The theoretical grain size of the surface composite layer is determined by the Zener-Holoman parameter.

The addition of Al_2O_3 particles to AZ91 alloy and fabrication of $\text{Al}_2\text{O}_3/\text{AZ91}$ nano surface composite using a square profiled FSP tool, rotating at 900 rpm speed and a traverse speed of 80 mm/min produced optimal results in a single FSP pass. It was observed that the grain size and the frictional temperature was reduced with a reduction in traverse speed. Also, higher traverse speed yielded a better distribution of the nano alumina particles and a decrease in grain size as per the Hall–Petch relationship. The evolved grain size could be related to Zener limiting grain size (d_z), which suggests that the dispersing of fine Al_2O_3 particles limits the grain growth, resulting in the formation of ultrafine grains in the nano surface composite. (Faraji *et al.*, 2011).

The incorporation of 40 nm size Al_2O_3 particles to the surface of AA7075 plates through FSP produced surface composite having enhanced hardness to the tune of double the original hardness after four FSP passes. (Refat *et al.*, 2016). Similarly while dispersing 50 nm-sized Al_2O_3 particles in 6082 aluminum alloy through FSP; the hardness increases 3 folds and a significant improvement in wear resistance was realized. This enhancement of hardness is attributed to strengthening mechanisms, viz. Orowan strengthening, grain and substructure strengthening, quench hardening caused by the dislocations generated to compensate the difference in thermal contraction between the matrix and the reinforcement particles, and work hardening effect caused by the mismatch in strain between the plastic matrix and the elastic reinforcement particles. The wear behavior of the matrix changed from abrasive to adhesive, whereas in the surface nanocomposite the wear is both adhesive and abrasive was attributed to the lowered coefficient of friction associated with reduced abrasive mode of wear (Shafiei-Zarghani *et al.*, 2009).

The multiple passes of FSP on nano sized Al_2O_3 of around 50 nm average particle size placed in shallow grooves resulted in finer grains in the Al matrix. The uniform dispersion of the nano Al_2O_3 particles yielded around three times increase in hardness. The Al/ Al_2O_3 nano surface layer (SCL) exhibits an abrasive mode of wear at loads of 20 and 40 N, whereas as the load increases to 60 N, the mode of wear is dominantly adhesive. (Shafiei-Zarghani *et al.*, 2011).

The coating of Al_2O_3 nanoparticles on Al2024 substrate through air plasma spraying and subjecting to FSP produces a surface nanocomposite having 600 μm penetration into the surface of the substrate. This surface nanocomposite exhibited enhanced bonding to substrate, hardness, and wear resistance. The wear mode involved delamination. (Zahmatkesh and Enayati, 2010).

The Cu/ SiC_p nanocomposite fabricated through the FSP route produced a 95% enhancement in the microhardness with the incorporation of 50 nm-sized SiC particles in the copper matrix. The frictional heat during FSP reached peak value with increased rotational speed and decreased with an increase in processing speed (traverse speed). The tool tilt angle had less influence on peak temperature when compared with rotational and processing speed. The hardness of the Cu/ SiC_p nano surface composite increased with a decrease in rotational speed and an increase in processing speed. Further, the hardness increased with the increase in tool tilt angle due to the effective dispersion of SiC_p particles and forging/compaction caused by stirring action during FSP (Srinivasan and Karunanithi, 2015).

In the FSP of 5052 aluminum sheets, the 5 μm and 50 nm-sized SiC particles were reinforced in to the substrate to yield an Al5052/SiC MMC. The change in the direction of the FSP tool rotation between the FSP passes, multiple passes and the associated decrease in size of SiC particles contributed to enhanced hardness and wear properties (Dolatkhah *et al.*, 2012).

The incorporation of nano-sized SiC reinforcement particles in AZ31 magnesium alloy substrate using increased tool rotational speed/advancing speed ratio produced good dispersion of nanoparticles in the Mg/SiC nanocomposite surface layer (Erfan and Kashani-Bozorg, 2011).

The Al5083/ B_4C surface composite layer (SCL) resisted wear in conformance with Archard's law which states that the volume loss in the AMC is inversely proportional to the hardness. ie, higher the hardness of the composite, lower shall be the wear rate; since the AMC shall resist the removal of material due to wear by virtue of high hardness imparted by the dispersion of nano B_4C through FSP and their good bonding with the matrix in the SCL and with the Al5083 substrate. The multiple passes of FSP enhanced the homogenous distribution of the B_4C reinforcement particles and resulted in increased hardness and formation of ultrafine grains (Yuvaraj *et al.*, 2015).

Multi-Walled Carbon Nano Tubes (MWCNT)/A1016 fabricated through FSP exhibited wettability between the hydrophilic MWCNT's and A1016 matrix. Breaking of the MWCNT occurred due to the high compressive forces prevailing during FSP. The presence of MWCNT interrupted the movement of dislocations caused due to a mismatch of elastic modulus and coefficient of thermal expansion between the aluminum matrix and MWCNT. With the increase in the volume fraction of MWCNT, the tensile strength and microhardness of MWCNT/A1016 composite increased at the cost of a reduction in elongation; which indicates that the addition of more MWCNT made the composite brittle (Liu *et al.*, 2013a).

In MWCNT/AZ31 surface composite, the dispersion of the MWCNT in the AZ31 matrix was influenced by the travel speed of the FSP tool. The uniform dispersion of the MWCNT promoted grain refinement to yield grains having less than 500 nm size. (Morisada *et al.*, 2006).

The Graphene/Aluminum surface composite was fabricated through FSP by carrying out FSP on 5052-H32 aluminum alloy sheets over which graphene oxide (GO)/water colloid was filled. Due to the frictional heat of the FSP, the GO reduced to a highly-conductive reduced GO (RGO) and thereby increasing the thermal conductivity and ductility of the MMC. (Jeon *et al.*, 2014). The strengthening mechanism in Graphene oxide (GO)/Al5083 surface composite involved grain boundaries and sub boundaries arresting dislocations and by the presence of GO or presence of reinforcing particles (Orowan theory). The mechanical properties improved, whereas the elongation reduced, which made the MMC brittle (Naghshhehkish *et al.*, 2019).

Nano Hydroxyapatite nHA/AZ31 FSPed surface composite was investigated as it has the benefits of an MMC having refined grains and embedding nHA in the magnesium alloy matrix for biomedical applications. The nHA enhances the biomineralization, wettability, corrosion resistance and thus making the FSPed MMC biocompatible. (Ratna Sunil *et al.*, 2014).

Surface Micro Composites

The FSPed surface composite (SC) formed by the addition of Al_2O_3 (AZ91/ Al_2O_3) and SiC (AZ91/SiC) to as-cast AZ91 magnesium alloy exhibited ultrafine-grained structure, good tensile strength and elongation, and improved distribution of the reinforcement particles with multiple FSP passes. The AZ91/SiC exhibited abrasive wear and delamination, whereas the AZ91/ Al_2O_3 exhibited delamination, which vanished with multiple passes of FSP. (Asadi *et al.*, 2011).

The Al1100 alloy reinforced with rice husk ash-derived, amorphous silica particles fabricated through FSP at a rotational speed of 1140 rpm, traveling speed of 45 mm/min, and a 2° tilt angle; exhibited 100% enhanced hardness. The silica particles disturbed the grain growth and caused grain refinement and reduced wear of the composite. (Zuhailawati *et al.*, 2016).

Instead of carrying out FSP on reinforcement particles filled in grooves or blind holes machined on the substrate, alternatively, the reinforcement particles can be deposited on the substrate through coating techniques. The Al_2O_3 particles of 10 μm size mixed with aluminum were coated on aluminum Al6061 substrate through cold gas dynamic spraying. The cold sprayed Al_2O_3 particles tend to segregate, which are dispersed uniformly in the MMC through FSP. The FSP of the MMC coatings decreased the reinforcement particle size, which causes a reduction in interparticle distance, i.e., the inter-particle mean free path. The reduction in inter-particle mean free path contributed to increased hardness in the MMC coating. (Hodder *et al.*, 2012). The inter-particle distance λ is expressed in the formula. (Kouzeli and Mortensen, 2002).

$$\lambda = (1 - V_p)/N_L \quad (4)$$

where

V_p is the volume fraction of the reinforcement particles and

N_L is the number of particles intercepted per unit length.

The surface composite fabricated on pure copper sheets by incorporating 25 μm SiC particles through FSP yielded a two-times increase in hardness. Further, the wear resistance and average friction coefficient were enhanced without any formation of intermetallic compounds. (Akramifard *et al.*, 2014).

The as-cast plates of AZ91 alloy subjected to FSP with the incorporation of 5 μm sized SiC particles yielded good grain refinement and enhanced hardness. The tool penetration depth (PD) greatly affected the quality of the surface composite formed through FSP. The PD is influenced by the FSP process parameters, namely traverse speed, rotational speed, and tilt angle. Generally, PD is measured as the distance from the first contact point of the tool shoulder and the workpiece surface. (Asadi *et al.*, 2010).

The fabrication of Cu/Si micro surface composites through FSP with an increase in traverse speed and a decrease in rotational speed caused a reduction in the grain size, enhanced hardness, higher average friction coefficient, and enhanced wear resistance. Whereas higher traverse speed resulted in, non-uniform distribution of SiC particles and reduction in hardness. (Barmouz *et al.*, 2011).

The fabrication of 10 μm mean diameter SiC_p particles reinforced thixoformed (TF) AZ91D alloy, surface composite layer through FSP yielded grain refinement in the nugget zone. Further grain refinement was observed in the thermomechanically affected zone (TMAZ) which is attributed mainly to dynamic recrystallization and, splitting and fracture (mechanical separation) of the primary grains. In TMAZ, strain and frictional heat increases with the increase of the number of the FSP passes (Chen *et al.*, 2010).

The Direct Friction Stir Processing (DFSP) uses a hollow-pin less DFSP tool, where the reinforcement particles flow into the enclosure between the concave tool shoulder and the substrate and get ironed into the workpiece through the rotating action of the DFSP tool. Satisfactory results were observed with just one FSP pass in the Mg/SiC_p surface composite. (Huang *et al.*, 2014).

The 5083Al alloy rolled plate surface added with micron sized SiC particles when subjected to FSP process produced surface composite layer of thickness 50–200 μm . With the incorporation of 0.7 μm average particle size of 27 vol% SiC on 5083 aluminum alloy, it was observed that as the tool traverse rate increases the bonding between the surface composite layer and the substrate is poor. (Mishra *et al.*, 2003).

As the FSP tool pin diameter is increased the diameter of the shoulder gets reduced. The shoulder being the source of frictional heat, the decrease in shoulder diameter due to an increase in pin diameter leads to the generation of less heat and formation of voids and defects in the stir zone (SZ) and clustering of SiC reinforcement particles in AA5083 alloy. The maximum temperature generated (T_{max}) in the stir zone (SZ) can be estimated by the expression

$$T_{\text{max}}/T_m = K(\omega^2/(v \times 10^4))^\alpha \quad (5)$$

Where

K is a constant having value between 0.65 and 0.75

ω is rotational speed in rpm

v is the traverse speed in inch/min

α is an exponent ranging from 0.04 to 0.06

T_m is the melting point of the alloy in $^\circ\text{C}$

The highest values of α and K yield an estimation of peak temperature. (Sharma *et al.*, 2015). Bulk surface composites could be fabricated by the dominant role of the shoulder of the FSP tool. The shoulder generates enough frictional heat to form a good bond in the SiC_p /5A06 composite layer and between the composite layer and the substrate. (Wang *et al.*, 2009).

The scattering of TiC particles during FSP of AZ31 alloy was prevented by using a pinless FSP tool which seals the top surface on the milled groove in the AZ31 alloy. The volume fraction of FSPed groove could be calculated from the expression. (Balakrishnan *et al.*, 2015).

$$\text{Volume fraction} = (\text{Area of groove}/\text{Projected area of tool pin}) \times 100 \quad (6)$$

Where,

$$\text{Area of groove} = \text{Groove width} \times \text{Groove depth} \quad (7)$$

and

$$\text{Projected area of tool pin} = \text{Pin diameter} \times \text{Pin length} \quad (8)$$

The fabrication of TiC/AA1050 surface composite through FSP was carried out on a V groove filled with TiC particles which were compressed and sealed to the V groove surface initially by a pinless FSP tool and subjected to FSP using a regular FSP tool having a pin. At low rotational speeds, insufficient frictional heat was produced which causes defects, and at high rotational speed the dilution of the TiC/Al resulted, causing a reduction in wear properties. (Akinlabi *et al.*, 2014). The AA6082/TiC surface composite exhibited enhanced wear properties and hardness attributed to the grain refinement caused by the addition of TiC particles and the FSP. The increased volume fraction of TiC reinforcement particles changes the mode of wear from adhesive wear to abrasive wear. These enhanced properties can be correlated to Archard's Law. (Thangarasu *et al.*, 2014).

The FSP of ZM21 magnesium alloy surface composite reinforced with B₄C and SiC indicated that the FSPed ZM21/B₄C surface composites are superior to the ZM21/SiC surface composite; having enhanced hardness and wear resistance. The B₄C and SiC carbide particles improve the hardness of the ZM21 surface composites through grain boundary pinning and dispersion hardening. The SiC and B₄C carbide powders change the wear behavior of ZM21 magnesium surface composite from an abrasive mode of wear to an adhesive mode of wear. (Madhusudhan Reddy *et al.*, 2013). The Cu/B₄C surface composite exhibited good distribution of the B₄C reinforcement particles and the formation of a higher area of surface composite on the Cu substrate. This was achieved with FSP parameter namely higher FSP tool rotational speed and lower processing speed which generated higher frictional heat and better material transportation associated with the increased stirring action of the FSP tool. The bonding of B₄C particles with the copper matrix and grain refinement was due to the pinning effect of the B₄C reinforcement particles. (Sathiskumar *et al.*, 2013).

Surface Hybrid Composites

The addition of CeO₂ and SiC in the Al5083 alloy matrix through FSP yielded hybrid nanocomposite possessing good grain refinement and homogeneous distribution of reinforcement particles. The Al5083/CeO₂/SiC surface hybrid composite (SHC) exhibited high wear resistance, lower friction co-efficient due to solid lubrication provided by CeO₂ particles. The wear mechanism in the Al5083 alloy was due to severe adhesive wear, whereas in the SHC it changed to abrasive wear and delamination. (Amra, Ranjbar and Hosseini, 2018). The SCs fabricated through FSP with the addition of SiC + Gr and SiC + Al₂O₃ to 6061-T6 aluminum alloy exhibited uniform distribution of the reinforcing particles in the nugget zone. The microhardness of Al-SiC/Al₂O₃ SC increased due to the presence of SiC and Al₂O₃ particles and their pinning effect. The Al-SiC/Gr SHC exhibited high wear resistance due to the presence of SiC which acts as a load-bearing element and Gr acts as a solid lubricant. Even though wear properties increased, the tensile properties decreased indicating that the material becomes brittle. (Aruri *et al.*, 2013).

The FSP of aluminum 6061-T6511 alloy with sub-micron-sized Al₂O₃ (200 nm nominal diameter) and SiC (300 nm nominal diameter) particles yielded hybrid surface composite up to 3 mm depth with the hard phases of around 20–30 vol%. The FSP resulted in a 40% reduction in friction and 90% reduction in wear, which is contributed to a high density of matrix dislocation caused by FSP. (Qu *et al.*, 2011).

The Al6063 surface hybrid composite fabricated using B₄C and SiO₂ reinforcement particles on the Al6063 substrate exhibited good grain refinement of an average grain size of 8 µm attributed to the multi-pass FSP. The combination of 30% SiO₂ and 70% B₄C to Al6063 resulted in decreased specific wear rate; whereas the SHC having 20% SiO₂ and 80% B₄C exhibited increased specific wear rate (Dinesh *et al.*, 2019).

The Al5083 SHC reinforced with multi-walled carbon nanotubes (MWCNT) and nano-sized cerium oxide particles in the volume ratio of 75–25 through FSP yielded maximum tensile strength and hardness value. The good dispersion of reinforcement particles in the nugget zone was achieved by using a threaded cylindrical hardened steel FSP tool rotating at speeds of 600 and 800 rpm and a travel speed of 35 and 45 mm/min and a 5° tilt. The incorporation of nano-sized cerium oxide increased the pitting resistance as it acts as a cathodic inhibitor. Multiple mechanisms come into play to strengthen the SHC viz., Orowan mechanism; and the existence of large coefficient of thermal expansion mismatch between the reinforcement particles and the aluminum matrix causing an increase in dislocations at the interface leading to work hardening of the matrix. Further the fragmentation and distribution of the large Al6(Mn, Fe) intermetallic particles during the multi-pass FSP process and the associated grain refinement led to enhancement of hardness due to Hall-Petch relation (Hosseini *et al.*, 2015).

The AA1050-H24 aluminum hybrid composite exhibited improved wear resistance with the addition of SiC and Al₂O₃ particles of 1.25 µm average size. The SHC was processed using an FSP tool having a square-shaped probe rotating at 1500 rpm and traveling at a speed of 1.66 mm/s. Except for the presence of some voids, the SHC had a uniform distribution of the reinforcement particles in the nugget zone. The average hardness decreased as the content of Al₂O₃ increased. The SHC having 80% SiC + 20% Al₂O₃ yielded good wear resistance (Mahmoud *et al.*, 2010).

AA6360/(TiC + B₄C) hybrid surface composite layers (SCLs) were fabricated through FSP with HCHCr steel, cylindrical threaded pin at a rotational speed of 1600 rpm, and a traverse speed of 60 mm/min and an axial thrust force of 8 kN. The FSP runs were done with two passes in opposite directions, which resulted in homogeneous distribution of TiC and B₄C particles in the AA6360 matrix. The SCLs having AA6360 50% TiC + 50% B₄C exhibited the least wear rate attributed to the fabrication of the

thin tribo film in the SCLs. The FSP enhanced the wear resistance and the strengthening mechanism enhancing the wear resistance is the combination of four processes namely, Orowan strengthening caused by the dispersion of fine reinforcement particles, strengthening due to grain refinement, quench hardening due to dislocations formed to compensate the differential thermal contraction between the matrix and the reinforcement and work hardening effect caused due to the mismatched strain between the plastic matrix and the elastic reinforcement particles. Further, the formation of oxide/tribo film from the dislodged particles acts as a solid lubricant and thus reducing the frictional coefficient and wear resistance. (Rejil *et al.*, 2012).

The wear behavior of AA6063-B₄C/TiB₂ hybrid surface improved when processed with a threaded FSP tool. The dynamically recrystallized zone (DRX) exhibited a reduction in grain size which is due to the increased dislocation density caused by the strain applied in the stir zone by the FSP tool. This grain size reduction combined with Orowan strengthening, caused by the dispersion of the reinforcement particles during FSP; improved the hardness of the MMC. The in situ formed TiB₂ particles exhibited enhanced bonding with the AA6063 matrix and contribute to the increased hardness and wear resistance. The hybrid surface composite when subjected to heat generated during wear, forms a mechanically mixed layer (MML) having a protective oxide film, like aluminum oxide or iron oxide that makes the wear become mild wear. (Narimani *et al.*, 2016).

In the hybrid metal matrix composite (HMMC) Al5083/Graphite/Al₂O_{3p}, a good distribution of reinforcement particles was observed, with the possibility of agglomeration with an increase in the volume fraction of the reinforcement particles. The HMMC having a 75% hybrid ratio (HR) of Graphite exhibited the least wear rate, whereas HMMC having 50% HR of Graphite possess good wear resistance and tensile strength. Hence the HR aids in designing the HMMC possessing the desirable properties. (Mostafapour Asl and Khandani, 2013).

The addition of carbon nanotube (CNT) and Al₂O₃ nanoparticles to the surface of Al5083 yielded a hybrid surface composite Al5083/CNT/Al₂O₃ nanocomposite. The Al₂O₃ nanoparticles got dispersed in intra-grain and grain boundaries, whereas the CNT got pinned into the grain boundaries when subjected to FSP. This behavior improved the hardness, tensile strength, and wear resistance. The presence of Al₂O₃ nanoparticles and CNT prevents the movement of dislocations and hence improves the hardness. (Ostovan *et al.*, 2020). The increased hardness conforms to the Archard equation, which states that these nanocomposites shall have better wear resistance. (Yang, 2003). The homogeneous distribution of the reinforcements leads to good interfacial bonding with the AA5083 matrix which prevents pull out during dry sliding. Further, the Al₂O₃ nanoparticles and CNT act as load barriers increases the hardness and minimizes plastic deformation. Even the damage caused to CNT during FSP, aids in the reduction of wear since the damaged CNT forms carbon films which act as a dry lubricant. (Ostovan *et al.*, 2020).

Surface-Powder Metallurgy In-Situ Composites/Intermetallic Powder Composite

The nano-sized AA7075 particles and TiC particles were packed in the groove milled on the surface of the AA7075 T651 alloy substrate. The wear rate reduction was observed. Whereas the reduction of hardness in the stir zone was observed in the T651 conditioned AA7075 alloy which losses its hardness upon plastic deformation caused by the FSP. (García-Vázquez *et al.*, 2016).

The 99% purity aluminum particles of 325 mesh size were mixed with 15% of 99.5% purity copper particles of 320 mesh size, to prepare the Al-15Cu alloy billet through the powder metallurgy route. This billet was sintered to give it sufficient strength to withstand the FSP passes. The Al-15Cu billet subjected to multiple passes of FSP formed in situ Al₂Cu intermetallic reinforcement which was distributed homogeneously in the aluminum matrix. The FSP passes and the Al₂Cu intermetallic reinforcement imparted good young's modulus, compressive strength, and compressive ductility. (Hsu *et al.*, 2005).

The Al-Cu and Al-Ti billets produced from the elemental metal powder mixtures, through powder metallurgy upon sintering get good structural strength to undergo FSP. The sintered billets undergo severe plastic deformation and the metal powders get homogeneously mixed and get a refined distribution of phases. A further exothermic reaction takes place between the aluminum and the transition metals Cu and Ti. Thus the high temperature created during the FSP and the exothermic reaction promotes the formation of intermetallic phases namely Al₂Cu and Al₃Ti, in situ during FSP. Further, the material undergoes hot consolidation to yield a fully dense material possessing high strength. The strength of the composite increased, with the increase in the content of the reinforcement. (Hsu *et al.*, 2007).

The addition of atomized aluminum powder with 10, 20, or 30 vol% denoted as Al-10Si, Al-20Si, or Al-30Si and processing through powder metallurgy route and upon sintering make the material resist the forces created during FSP. Multiple passes of FSP produced Al-Si composite led to good strength and ductility. This can be attributed to the homogeneous distribution of silicon particles and the formation of ultrafine-grained aluminum matrix. The composite displayed compressive yield strength higher than the tensile strength due to residual stress developed during FSP. The young's modulus of the composite conforms to the Halpin-Tsai equation. (Hull and Clyne, 1996). The presence of few nanosized silicon particles within the aluminum grain interacts with the dislocations moving within the aluminum grains and thus contribute to the strengthening by the Orowan mechanism. (Lee *et al.*, 2011).

The Carbon Nanotube (CNT), Al, and CNT/6061 Al powder after cold compacting when subjected to degassing and vacuum hot pressing and hot forging were subjected to multiple passes of FSP. The combined powder metallurgy processing and FSP of CNT and aluminum, CNT/Al, and CNT/6061Al produce a composite that displayed good tensile strength and electrical conductivity. During artificial aging treatment of CNT/6061 Al the Si and Mg tend to segregate at the CNT-Al interface and contributed to the increase in electrical conductivity of CNT/6061 Al; whereas the addition of CNT in CNT/Al decreased the electrical conductivity. (Liu *et al.*, 2014). The 1.5–4.5 vol% CNT/2007Al AMC produced through powder metallurgy route, yielded uniform distribution of the carbon nanotubes (CNT) when subjected to multiple overlapping FSP passes. The FSPed CNT formed good

bonding with the aluminum matrix. No carbides were formed but Al_4C_3 phase was formed at the tips of the CNTs as carbon atoms are reactive in the tips. These tips are the outcome of the shortening of the CNTs when subjected to the shear strain during FSP, but the CNTs did not lose their structural integrity and thus there is no formation of any stress concentration. The FSP dispersed the CNT in the matrix. To further improve the tensile strength and elongation, the CNTs have to be aligned by subjecting to processing like rolling. (Liu *et al.*, 2013b).

Surface Metal Powder Composites/Surface Composites SCs

The surface metal matrix composite with the inclusion of metal powders like nano Mg powder on pure zinc plate was carried out through the FSP route. The synthesized surface MMC induces grain refinement due to dynamic recrystallization and increases the hardness of the pure zinc substrate and thus making the material an ideal candidate for biodegradable orthopedic implants. The deposition of metal powder in blind holes arranged in a zig-zag formation, instead of in a groove reduces the risk of agglomeration of the metal particles during the friction stir processing (Singh *et al.*, 2019).

The fabrication of Ti6Al4V (TC4)/Zinc (Zn) surface nano composite through FSP was carried out for surface modification of TC4, to promote the osteogenic performance of the dental and orthopedic implants. The presence of Zn particles in the SC enhances the hydrophilicity thus improving the biocompatibility in terms of cell adhesion and cell proliferation. The Zn particles were filled inside holes of depth 1 mm and 0.5 mm. The FSP of TC4/Zn caused severe plastic deformation leading to the formation of numerous nanocrystalline β regions, grain boundary α phase, fine acicular martensite α' , and coarse acicular α phase. This grain refinement caused an increased surface hardness and a decreased elastic modulus in the SC. (Zhu *et al.*, 2018).

The formation of SC by the inclusion of 99.9% purity Nickel particles of 1–3 μm diameter, in A413 alloy and situ formation of Al_3Ni intermetallic particles, improved the wear behavior of the A413 alloy. The increase in the number of passes of FSP improved the distribution of the reinforcement particles and increased the intermetallic phases, which imparted wear resistance to the A413 alloy. (Golmohammadi *et al.*, 2015).

The FSP of AA7050-T7451 age-hardened alloy was carried out with the addition of hybrid particles namely Al_2O_3 , TiB_2 , Zn, and Mg. The study showed that the microhardness of the AA7050 alloy increased upon subjecting to FSP. The friction stir welding of the SC fabricated through FSP yielded an improvement in hardness. The increase in hardness of the friction stir processed SC was attributed to the material being subjected to the pass of the FSW tool which is similar to the effect produced by the multiple passes of the FSP tool. (Gangil *et al.*, 2019).

The addition of Molybdenum (Mo) to Al6082 aluminum alloy through FSP, produced SC with improved ductility. The SC exhibited a homogenous distribution of the molybdenum within the stir zone and grain refinement due to the pinning effect of the Mo particles and dynamic recrystallization. The SC improved strength without the loss of ductility, due to the good bonding of Mo particles with the Al6082 matrix and lack of interfacial reaction. (Selvakumar *et al.*, 2017).

Surface Bulk Composites

The semi-solid cast (compcast) AA2024/1 wt% Al_2O_3 nano AMC was FSPed under FSP tool rotational speed of 400 rpm and tool traverse of 20 mm/min. The FSP resulted in uniform distribution of the Al_2O_3 nano reinforcement particles, grain refinement in the AA2024 matrix, and enhanced hardness, strength, and ductility. The casting defects like porosity and shrinkage cavities were eliminated in the process of making surface nanocomposite through FSP. (Hoziefa *et al.*, 2016). The cast Al-Si alloy (A356) when FSPed yielded a microstructure with fine Si particles of size 0.25–0.42 μm . A banded structure was observed at lower tool rotational speeds/traverse speed ratios, exhibiting a low density of coarse particles in the nugget zone. The bonded structure disappeared associated with homogenous distribution of fine Si particles in the nugget zone, at higher tool rotational speeds/traverse speed ratios. (Ma *et al.*, 2006). The as-cast Al-TiC in situ composites were FSPed at a rotational speed of 1000 rpm and traverse speed of 60 mm/min to yield a defect-free stir zone having homogenized refined grained nugget zone. The mechanical properties were enhanced with the formation of dynamically recrystallized equiaxed grain structure upon subjecting to FSP. (Bauri, 2014).

Concluding Remarks

The friction stir welding (FSW) a solid-state welding technique spawned friction stir processing (FSP) a new surface engineering technique. Like friction stir welding, friction stir processing is a green technology that is aggressively researched nowadays. Conventional surface engineering techniques rely on forming a coating of protective coating which could resist wear, corrosion, etc. The friction stir processing forms a metal matrix composite (MMC) layer which becomes an integral part of the substrate metal/alloy/MMC. The virtue of imparting the properties of MMC namely high hardness, wear-resistance, and functional properties makes FSP a promising technology for a variety of applications. Currently, the FSW tool is used to execute the FSP. There is a need to customize the FSP tool to make the process scalable to widely apply in industries and real-time applications. Most of the FSP studies have been carried out on aluminum matrix composites (AMC). As magnesium-based alloys and composites are emerging in various applications there is the scope and need to study friction stir processing of these materials.

References

- Akinlabi, E.T., *et al.*, 2014. Processing parameters influence on wear resistance behaviour of friction stir processed Al-TiC composites. *Advances in Materials Science and Engineering*. Article ID 724590, 12. <https://doi.org/10.1155/2014/724590>.
- Akramifard, H.R., *et al.*, 2014. Microstructure and mechanical properties of Cu/SiC metal matrix composite fabricated via friction stir processing. *Materials and Design* 54, 838–844. <https://doi.org/10.1016/j.matdes.2013.08.107>.
- Amra, M., Ranjbar, K., Hosseini, S.A., 2018. Microstructure and wear performance of Al5083/CeO₂/SiC mono and hybrid surface composites fabricated by friction stir processing. *Transactions of Nonferrous Metals Society of China* 28 (5), 866–878. [https://doi.org/10.1016/S1003-6326\(18\)64720-X](https://doi.org/10.1016/S1003-6326(18)64720-X).
- Ardell, A.J., 1985. Precipitation hardening. *Metallurgical Transactions A* 16 (12), 2131–2165. <https://doi.org/10.1007/BF02670416>.
- Arora, H.S., Singh, H., Dhindaw, B.K., 2012. Composite fabrication using friction stir processing – A review. *The International Journal of Advanced Manufacturing Technology* 61 (9), 1043–1055. <https://doi.org/10.1007/s00170-011-375di>.
- Aruri, D., *et al.*, 2013. Wear and mechanical properties of 6061-T6 aluminum alloy surface hybrid composites [(SiC + Gr) and (SiC + Al₂O₃)] fabricated by friction stir processing. *Journal of Materials Research and Technology* 2 (4), 362–369. <https://doi.org/10.1016/j.jmrt.2013.10.004>.
- Asadi, P., *et al.*, 2011. Experimental investigation of magnesium-base nanocomposite produced by friction stir processing: Effects of particle types and number of friction stir processing passes. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science* 42 (9), 2820–2832. <https://doi.org/10.1007/s11661-011-0698-8>.
- Asadi, P., Faraji, G., Besharati, M.K., 2010. Producing of AZ91/SiC composite by friction stir processing (FSP). *International Journal of Advanced Manufacturing Technology* 51, 247–260. <https://doi.org/10.1007/s00170-010-2600-z> (1–4).
- Ashjari, M., Mostafapour Asl, A., Rouhi, S., 2015. Experimental investigation on the effect of process environment on the mechanical properties of AA5083/Al₂O₃ nanocomposite fabricated via friction stir processing. *Materials Science and Engineering A* 645, 40–46. <https://doi.org/10.1016/j.msea.2015.07.093>.
- Avetand-Fénoël, M.-N., *et al.*, 2014. Characterization of oxide dispersion strengthened copper based materials developed by friction stir processing. *Materials & Design* 60, 343–357. <https://doi.org/10.1016/j.matdes.2014.04.012>.
- Azizieh, M., Kokabi, A.H., Abachi, P., 2011. Effect of rotational speed and probe profile on microstructure and hardness of AZ31/Al₂O₃ nanocomposites fabricated by friction stir processing. *Materials and Design* 32 (4), 2034–2041. <https://doi.org/10.1016/j.matdes.2010.11.055>.
- Balakrishnan, M., *et al.*, 2015. Synthesis of AZ31/TiC magnesium matrix composites using friction stir processing. *Journal of Magnesium and Alloys* 3 (1), 76–78. <https://doi.org/10.1016/j.jma.2014.12.007>.
- Barmouz, M., Besharati Givi, M.K., Seyfi, J., 2011. On the role of processing parameters in producing Cu/SiC metal matrix composites via friction stir processing: Investigating microstructure, microhardness, wear and tensile behavior. *Materials Characterization* 62 (1), 108–117. <https://doi.org/10.1016/j.matchar.2010.11.005>.
- Bauri, R., 2014. Optimization of process parameters for friction stir processing (FSP) of Al-TiC in situ composite. *Bulletin of Materials Science* 37 (3), 571–578. <https://doi.org/10.1007/s12034-014-0692-z>.
- Chang, C.I., Lee, C.J., Huang, J.C., 2004. Relationship between grain size and Zener-Holloman parameter during friction stir processing in AZ31 Mg alloys. *Scripta Materialia* 51 (6), 509–514. <https://doi.org/10.1016/j.scriptamat.2004.05.043>.
- Chen, T., *et al.*, 2010. Friction stir processing of thixoformed AZ91D magnesium alloy and fabrication of surface composite reinforced by SiCps. *Journal Wuhan University of Technology, Materials Science Edition* 25 (2), 223–227. <https://doi.org/10.1007/s11595-010-2223-0>.
- Dinesh, D., *et al.*, 2019. Evaluation of microstructure and tribological characterization of friction stir processed Al 6063 / B4C + SiO₂ composites. *AIP Conference Proceedings* 2128. <https://doi.org/10.1063/1.5117942>.
- Dolatkhah, A., *et al.*, 2012. Investigating effects of process parameters on microstructural and mechanical properties of Al5052/SiC metal matrix composite fabricated via friction stir processing. *Materials and Design* 37, 458–464. <https://doi.org/10.1016/j.matdes.2011.09.035>.
- Erfan, Y., Kashani-Bozorg, S.F., 2011. Fabrication of Mg/SiC nanocomposite surface layer using friction stir processing technique. *International Journal of Nanoscience* 10 (4–5), 1073–1076. <https://doi.org/10.1142/S0219581x11008538>.
- Faraji, G., Dastani, O., Akbari Mousavi, S.A.A., 2011. Microstructures and mechanical properties of Al₂O₃/AZ91 surface nanocomposite layer produced by friction stir processing. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture* 225 (8), 1331–1345. <https://doi.org/10.1177/2041297510393584>.
- Gandra, J., *et al.*, 2013. Wear characterization of functionally graded Al–SiC composite coatings produced by friction surfacing. *Materials & Design* 52, 373–383. <https://doi.org/10.1016/j.matdes.2013.05.059>.
- Gandra, J., *et al.*, 2014. Friction surfacing – A review. *Journal of Materials Processing Technology* 214 (5), 1062–1093. <https://doi.org/10.1016/j.jmatprotec.2013.12.008>.
- Gangil, N., *et al.*, 2019. Investigation on friction stir welding of hybrid composites fabricated on Al–Zn–Mg–Cu alloy through friction stir processing. *Journal of Materials Research and Technology* 8 (5), 3733–3740. <https://doi.org/10.1016/j.jmrt.2019.06.033>.
- García-Vázquez, F., *et al.*, 2016. Efeito dos parâmetros do processo de fricção agitação para reforçar uma placa de alumínio Al7075-T651 com TiC. *Soldagem e Inspecao* 21 (4), 508–516. <https://doi.org/10.1590/0104-9224/S12104.10>.
- Golmohammadi, M., Atapour, M., Ashrafi, A., 2015. Fabrication and wear characterization of an A413/Ni surface metal matrix composite fabricated via friction stir processing. *Materials and Design* 85. <https://doi.org/10.1016/j.matdes.2015.06.090>.
- Hodder, K.J., *et al.*, 2012. Fabrication of aluminum-alumina metal matrix composites via cold gas dynamic spraying at low pressure followed by friction stir processing. *Materials Science and Engineering A* 556, 114–121. <https://doi.org/10.1016/j.msea.2012.06.066>.
- Hosseini, S.A., *et al.*, 2015. Fabrication of Al5083 surface composites reinforced by CNTs and cerium oxide nano particles via friction stir processing. *Journal of Alloys and Compounds* 622, 725–733. <https://doi.org/10.1016/j.jallcom.2014.10.158>.
- Hoziefa, W., *et al.*, 2016. Influence of friction stir processing on the microstructure and mechanical properties of a compocast AA2024–Al₂O₃ nanocomposite. *Materials and Design* 106, 273–284. <https://doi.org/10.1016/j.matdes.2016.05.114>.
- Hsu, C.J., Kao, P.W., Ho, N.J., 2005. Ultrafine-grained Al–Al₂Cu composite produced in situ by friction stir processing. *Scripta Materialia* 53 (3), 341–345. <https://doi.org/10.1016/j.scriptamat.2005.04.006>.
- Hsu, C.J., Kao, P.W., Ho, N.J., 2007. Intermetallic-reinforced aluminum matrix composites produced in situ by friction stir processing. *Materials Letters* 61 (6), 1315–1318. <https://doi.org/10.1016/j.matlet.2006.07.021>.
- Huang, Y., *et al.*, 2014. Microstructure and surface mechanical property of AZ31 Mg/SiCp surface composite fabricated by direct friction stir processing. *Materials and Design* 59, 274–278. <https://doi.org/10.1016/j.matdes.2014.02.067>.
- Hull, D., Clyne, T.W., 1996. *An Introduction to Composite Materials*. Cambridge University Press. <http://doi.org/10.1017/CB09781139170130>.
- Jeon, C.H., *et al.*, 2014. Material properties of graphene/aluminum metal matrix composites fabricated by friction stir processing. *International Journal of Precision Engineering and Manufacturing* 15 (6), 1235–1239. <https://doi.org/10.1007/s12541-014-0462-2>.
- Jiang, Y., *et al.*, 2013. Nano-SiO₂ particles reinforced magnesium alloy produced by friction stir processing. *Reviews on Advanced Materials Science* 33 (1), 29–32.
- Khodabakhshi, F., Kokabi, A.H., Simchi, A., 2017. Reactive friction-stir processing of nanocomposites: Effects of thermal history on microstructure–mechanical property relationships. *Materials Science and Technology* 33 (15), 1776–1789. <https://doi.org/10.1080/02670836.2017.1318244>.
- Kouzeili, M., Mortensen, A., 2002. Size dependent strengthening in particle reinforced aluminium. *Acta Materialia* 50 (1), 39–51. [https://doi.org/10.1016/S1359-6454\(01\)00327-5](https://doi.org/10.1016/S1359-6454(01)00327-5).
- Lee, C.J., Huang, J.C., Hsieh, P.J., 2006. Mg based nano-composites fabricated by friction stir processing. *Scripta Materialia* 54 (7), 1415–1420. <https://doi.org/10.1016/j.scriptamat.2005.11.056>.

- Lee, I.S., *et al.*, 2011. Particle-reinforced aluminum matrix composites produced from powder mixtures via friction stir processing. *Composites Science and Technology* 71 (5), 693–698. <https://doi.org/10.1016/j.compscitech.2011.01.013>.
- Li, B., *et al.*, 2013. Fabrication of TiCp/Ti–6Al–4V surface composite via friction stir processing (FSP): Process optimization, particle dispersion-refinement behavior and hardening mechanism. *Materials Science and Engineering A* 574, 75–85. <https://doi.org/10.1016/j.msea.2013.03.019>.
- Lim, D.K., Shibayanagi, T., Gerlich, A.P., 2009. Synthesis of multi-walled CNT reinforced aluminium alloy composite via friction stir processing. *Materials Science and Engineering A* 507 (1), 194–199. <https://doi.org/10.1016/j.msea.2008.11.067>.
- Liu, Q., *et al.*, 2013a. Microstructure and mechanical property of multi-walled carbon nanotubes reinforced aluminum matrix composites fabricated by friction stir processing. *Materials and Design* 45, 343–348. <https://doi.org/10.1016/j.matdes.2012.08.036>.
- Liu, Z.Y., *et al.*, 2013b. Developing high-performance aluminum matrix composites with directionally aligned carbon nanotubes by combining friction stir processing and subsequent rolling. *Carbon* 62, 35–42. <https://doi.org/10.1016/j.carbon.2013.05.049>.
- Liu, Z.Y., *et al.*, 2014. Tensile strength and electrical conductivity of carbon nanotube reinforced aluminum matrix composites fabricated by powder metallurgy combined with friction stir processing. *Journal of Materials Science and Technology* 30 (7), 649–655. <https://doi.org/10.1016/j.jmst.2014.04.016>.
- Ma, Z.Y., Sharma, S.R., Mishra, R.S., 2006. Effect of friction stir processing on the microstructure of cast A356 aluminum. *Materials Science and Engineering A* 433 (1–2), 269–278. <https://doi.org/10.1016/j.msea.2006.06.099>.
- Madhusudhan Reddy, G., Sambasiva Rao, A., Srinivasa Rao, K., 2013. Friction stir processing for enhancement of wear resistance of ZM21 magnesium alloy. *Transactions of the Indian Institute of Metals* 66 (1), 13–24. <https://doi.org/10.1007/s12666-012-0163-4>.
- Mahmoud, E.R.I., *et al.*, 2010. Wear characteristics of surface-hybrid-MMCs layer fabricated on aluminum plate by friction stir processing. *Wear* 268 (9–10), 1111–1121. <https://doi.org/10.1016/j.wear.2010.01.005>.
- Martin, J.W., Doherty, R.D., Cantor, B., 1997. *Stability of Microstructure in Metallic Systems*. Cambridge University Press. (Cambridge Solid State Science Series BT - Stability of Microstructure in Metallic Systems).
- Meng, C., *et al.*, 2013. Evolution behavior of TiB₂ particles during laser welding on aluminum metal matrix composites reinforced with particles. *Transactions of Nonferrous Metals Society of China* 23 (6), 1543–1548. [https://doi.org/10.1016/S1003-6326\(13\)62628-X](https://doi.org/10.1016/S1003-6326(13)62628-X).
- Miranda, R.M., *et al.*, 2013. Reinforcement strategies for producing functionally graded materials by friction stir processing in aluminium alloys. *Journal of Materials Processing Technology* 213 (9), 1609–1615. <https://doi.org/10.1016/j.jmatprotec.2013.03.022>.
- Mishra, R.S., Ma, Z.Y., Charit, I., 2003. Friction stir processing: A novel technique for fabrication of surface composite. *Materials Science and Engineering A* 341 (1–2), 307–310. [https://doi.org/10.1016/S0921-5093\(02\)00199-5](https://doi.org/10.1016/S0921-5093(02)00199-5).
- Morisada, Y., *et al.*, 2006. MWCNTs/AZ31 surface composites fabricated by friction stir processing. *Materials Science and Engineering A* 419 (1–2), 344–348. <http://doi.org/10.1016/j.msea.2006.01.016>.
- Mostafapour Asl, A., Khandani, S.T., 2013. Role of hybrid ratio in microstructural, mechanical and sliding wear properties of the Al5083/Graphite p/Al20 3p a surface hybrid nanocomposite fabricated via friction stir processing method. *Materials Science and Engineering A* 559, 549–557. <https://doi.org/10.1016/j.msea.2012.08.140>.
- Naghshkehsh, N., *et al.*, 2019. Effect of graphene oxide and friction stir processing on microstructure and mechanical properties of Al5083 matrix composite. *Materials Research Express* 6(10), 106566. doi:10.1088/2053-1591/ab3a6f.
- Narimani, M., Lotfi, B., Sadeghian, Z., 2016. Evaluation of the microstructure and wear behaviour of AA6063-B4C/TiB₂ mono and hybrid composite layers produced by friction stir processing. *Surface and Coatings Technology* 285, 1–10. <https://doi.org/10.1016/j.surfcoat.2015.11.015>.
- Navazani, M., Dehghani, K., 2016. Fabrication of Mg-ZrO₂ surface layer composites by friction stir processing. *Journal of Materials Processing Technology* 229, 439–449. <https://doi.org/10.1016/j.jmatprotec.2015.09.047>.
- Ostovan, F., *et al.*, 2020. Fabrication of Al5083 surface hybrid nanocomposite reinforced by CNTs and Al₂O₃ nanoparticles using friction stir processing. *Journal of Composite Materials* 54 (8), 1107–1117. <https://doi.org/10.1177/0021998319874849>.
- Pantelis, D., *et al.*, 1995. Formation of wear resistant Al–SiC surface composite by laser melt–particle injection process. *Materials Science and Technology* 11 (3), 299–303. <https://doi.org/10.1179/mst.1995.11.3.299>.
- Qu, J., *et al.*, 2011. Improving the tribological characteristics of aluminum 6061 alloy by surface compositing with sub-micro-size ceramic particles via friction stir processing. *Wear* 271 (9–10), 1940–1945. <https://doi.org/10.1016/j.wear.2010.11.046>.
- Ratna Sunil, B., *et al.*, 2014. Nano-hydroxyapatite reinforced AZ31 magnesium alloy by friction stir processing: A solid state processing for biodegradable metal matrix composites. *Journal of Materials Science: Materials in Medicine* 25 (4), 975–988. <https://doi.org/10.1007/s10856-013-5127-7>.
- Refat, M., *et al.*, 2016. The effect of heat treatment on the properties of friction stir processed AA7075-O with and without nano alumina additions. In: Mishra, R.S., Mahoney, M.W., Sato, Y., Hovanski, Y. (Eds.), *Friction Stir Welding and Processing VIII*. Springer, pp. 115–123. https://doi.org/10.1007/978-3-319-48173-9_13.
- Rejil, C.M., *et al.*, 2012. Microstructure and sliding wear behavior of AA6360/(TiC + B₄C) hybrid surface composite layer synthesized by friction stir processing on aluminum substrate. *Materials Science and Engineering A* 552, 336–344. <https://doi.org/10.1016/j.msea.2012.05.049>.
- Sathiskumar, R., *et al.*, 2013. Role of friction stir processing parameters on microstructure and microhardness of boron carbide particulate reinforced copper surface composites. *Sadhana – Academy Proceedings in Engineering Sciences* 38 (6), 1433–1450. <https://doi.org/10.1007/s12046-013-0184-7>.
- Selvakumar, S., *et al.*, 2017. Characterization of molybdenum particles reinforced Al6082 aluminum matrix composites with improved ductility produced using friction stir processing. *Materials Characterization* 125, 13–22. <https://doi.org/10.1016/j.matchar.2017.01.016>.
- Shafiei-Zarghani, A., Kashani-Bozorg, S.F., Zarei-Hanzaki, A., 2009. Microstructures and mechanical properties of Al/Al₂O₃ surface nano-composite layer produced by friction stir processing. *Materials Science and Engineering A* 500 (1–2), 84–91. <https://doi.org/10.1016/j.msea.2008.09.064>.
- Shafiei-Zarghani, A., Kashani-Bozorg, S.F., Hanzaki, A.Z., 2011. Wear assessment of Al/Al₂O₃ nano-composite surface layer produced using friction stir processing. *Wear* 270 (5–6), 403–412. <https://doi.org/10.1016/j.wear.2010.12.002>.
- Sharma, V., Prakash, U., Kumar, B.V.M., 2015. Surface composites by friction stir processing: A review. *Journal of Materials Processing Technology* 224, 117–134. <https://doi.org/10.1016/j.jmatprotec.2015.04.019>.
- Singh, G.K., Verma, S., Misra, J.P., 2019. Development of Zn-Mg in Situ Composite using Friction Stir Processing. *Journal of Material Science and Mechanical Engineering* 6 (3), 160–162.
- Srinivasan, C., Karunaniithi, M., 2015. Fabrication of surface level Cu/SiCp nanocomposites by friction stir processing route. *Journal of Nanotechnology*. Article ID 612617, 10. <https://doi.org/10.1155/2015/612617>.
- Thangarasu, A., Murugan, N., Dinaharan, I., 2014. Production and wear characterization of AA6082-TiC surface composites by friction stir processing. *Procedia Engineering* 97, 590–597. <https://doi.org/10.1016/j.proeng.2014.12.287>.
- Wang, W., *et al.*, 2009. A novel way to produce bulk SiCp reinforced aluminum metal matrix composites by friction stir processing. *Journal of Materials Processing Technology* 209 (4), 2099–2103. <https://doi.org/10.1016/j.jmatprotec.2008.05.001>.
- Yang, L.J., 2003. Wear coefficient equation for aluminium-based matrix composites against steel disc. *Wear* 255 (1), 579–592. [https://doi.org/10.1016/S0043-1648\(03\)00191-1](https://doi.org/10.1016/S0043-1648(03)00191-1).
- Yuvaraj, N., Aravindan, S., Vipin, 2015. Fabrication of Al5083/B₄C surface composite by friction stir processing and its tribological characterization. *Journal of Materials Research and Technology* 4 (4), 398–410. <https://doi.org/10.1016/j.jmrt.2015.02.006>.

- Zahmatkesh, B., Enayati, M.H., 2010. A novel approach for development of surface nanocomposite by friction stir processing. *Materials Science and Engineering A* 527 (24–25), 6734–6740. <https://doi.org/10.1016/j.msea.2010.07.024>.
- Zhu, C., *et al.*, 2018. Microstructures, mechanical, and biological properties of a novel Ti-⁶V-⁴V/zinc surface nanocomposite prepared by friction stir processing. *International Journal of Nanomedicine* 13, 1881–1898. <https://doi.org/10.2147/IJN.S154260>.
- Zuhailawati, H., *et al.*, 2016. Mechanical properties of friction stir processed 1100 aluminum reinforced with rice husk ash silica at different rotational speeds. *International Journal of Metallurgical & Materials Engineering* 2 (1), 2–7. <https://doi.org/10.15344/2455-2372/2016/120>.

An Insight Into Processing Maps of Metal Matrix Composites

Biranchi N Sahoo, Sardar Vallabhbhai National Institute of Technology, Surat, Gujarat, India
Sushanta K Panigrahi, Indian Institute of Technology Madras, Chennai, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

The metal matrix composites (MMCs) are designed by considering the combined effect of metals and ceramics. Metals have moderate strength and ductility with low stiffness and low thermal stability. Whereas, ceramics are having high-temperature resistance along with high stiffness and high strength. The high strength, high modulus reinforcement particles provide an intermediate mechanical property between ductile matrix and hard reinforcement in MMCs. The MMCs with ceramic particle reinforcements demonstrate superior properties in strength, elastic properties, resistance to wear, creep and fatigue as compared to unreinforced matrix material, which makes them promising for structural application in automobile and aerospace industries.

The developed MMCs can further be exposed to various manufacturing processes such as forging, rolling or extrusion while fabrication of products for end-use applications. The manufacturability of most of these manufacturing processes highly depend on the different manufacturing process parameters like strain rate, strain and temperature (Sahoo and Panigrahi, 2019a; Zang *et al.*, 2019; Xu *et al.*, 2018b). Hence, for safe and efficient deformation of MMCs, it is important to establish the range of manufacturing process parameters like strain rate, strain and temperature etc. The ease of active defect-free deformation is called a material's workability.

The workability is defined as the ease of deformation of material for a particular metalworking process without any defect. The defects are generally in the form of shear band, local necking and surface irregularity which occurs during different types of metalworking processes. Both the material characters (such as grain morphology, second phase distribution and geometry of the sample) and process parameters (like strain, strain rate and temperature) affect the workability of materials. For cold working process, material characters are more important than the process parameters for deciding the workability because of inactive metallurgical phenomenon. However, for hot working, both the material characters as well as process parameters are important for workability.

The fundamental behavior of materials can be studied by optimizing the workability under different processing environments. Several researchers have been attempting to understand the flow behavior of materials during deformation through consequence of processing parameters (Liu *et al.*, 2019; Mokdad *et al.*, 2017; Wang *et al.*, 2016; Selvam *et al.*, 2015). They have established different maps for describing the deformation behavior and mode of fractures that arise during deformation.

Ashby developed a map by plotting the normalized shear stress against absolute temperature (Langdon and Mohamed, 1978). Fig. 1 represents a schematic diagram of an Ashby map, which is plotted by taking logarithmic of normalized stress ($\frac{\sigma}{G}$) in y axis and homologous temperature ($\frac{T}{T_m}$) in X axis. Where σ represents the stress applied, G stands for shear modulus, T signifies the temperature value, and T_m represents melting temperature of material in degrees Kelvin. The map is divided into three zones: (1) The first zone is represented by a horizontal line, ($\frac{\sigma}{G} \sim 4 \times 10^{-2}$) which signifies the material's ideal strength; (2) The second zone is at normalized stress (varies between $4 \times 10^{-3} - 4 \times 10^{-2}$) where the material deforms by the conventional motion of dislocations by means of glide through the lattice; and (3) The third zone is at stress values of $\frac{\sigma}{G} < 4 \times 10^{-3}$, where deformation behavior transform to diffusion-controlled creep processes (i.e., Nabarro-Herring diffusional creep and Coble diffusional creep).

Raj (1981) developed maps exhibiting an immense range of strain rate and temperature domains. This map is plotted by taking temperature in horizontal-axis and strain rate in vertical-axis. The boundaries in map created by Raj represent the existence of different microscopic phenomena (such as ductile fracture, adiabatic shear, dynamic recrystallization) in materials during deformation. The boundaries of temperature and strain rates are estimated by appropriate equations for these various microscopic phenomena. The areas confined through these boundaries are the domains in which the particular microscopic aspect will succeed during deformation. The map also shows a safe region which indicates the occurrence of defect-free manufacturing zone/region at certain set of processing/manufacturing parameters. Fig. 2 represent an example of Raj Map for austenitic stainless steel.

Ashby and Raj maps are valid for steady states as they have used shear strain rate equations. The equations used in Ashby and Raj maps are dependent on basic atomic mechanism such as grain boundary sliding, diffusion dislocation motion, twinning and phase transformations. The maps are valid for pure metals and cannot be applied to alloys and MMCs due to difficulties in identifying different atomistic mechanisms appropriately.

Concept of Processing Map

The hot workability of pure metals, alloys and MMCs can be analyzed by means of the processing map. A processing map is an explicit depiction of a material's response to the process parameters for finding optimum conditions for workability and to attain microstructural control in the materials. Processing map is also an important tool to design processing steps to attain maximum product yield, reproducible microstructure and mechanical properties in the material. Many material-based models have been

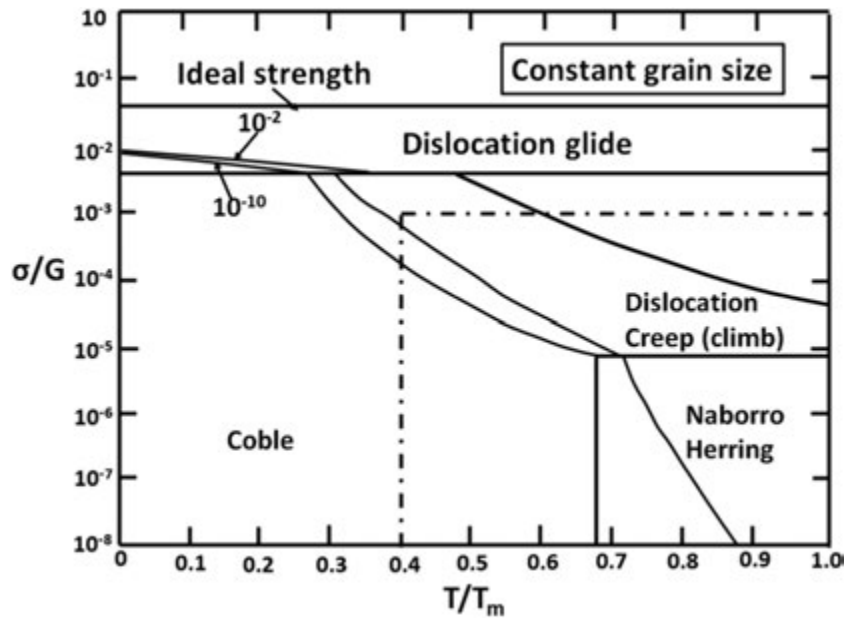


Fig. 1 Schematic diagram for Ashby map.

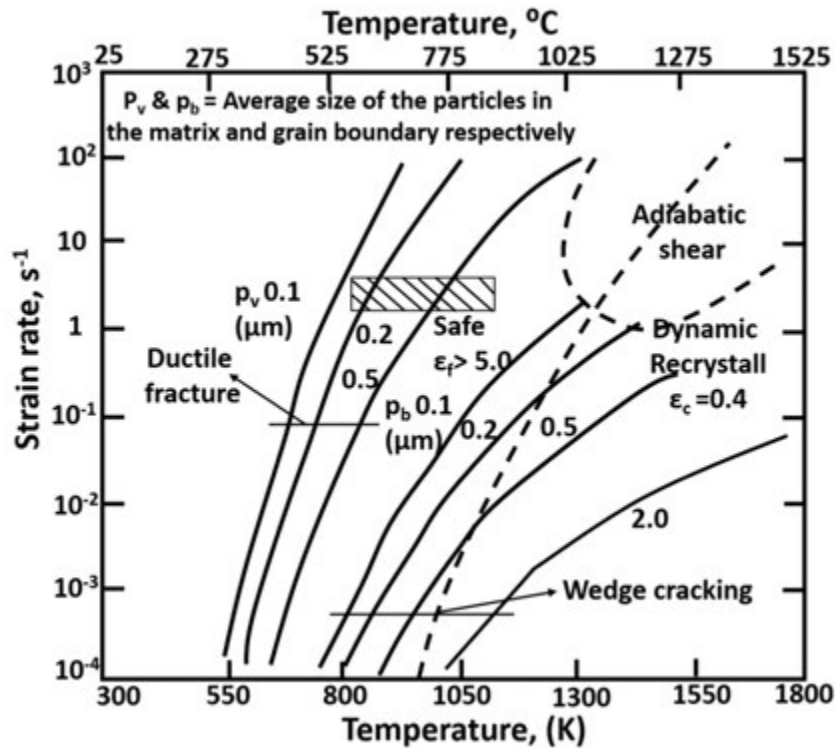


Fig. 2 Schematic diagram represents Raj map for austenitic stainless steel.

established to analyze the hot deformation behavior of the materials. The three most prominent developed models are: (1) Kinetic model, (Jonas *et al.*, 1969) (2) Atomistic model, (Raj, 1981) and (3) Dynamic materials modeling (DMM) (Prasad *et al.*, 1984).

Kinetic and atomistic models are only concisely discussed here as they form the base for the investigation of constitutive behavior; however, the processing maps will be conferred in details.

Kinetic Model

Kinetic model predicts the deformation mechanism by the help of strain hardening exponent (n) and activation energy (Q). The hot deformation mechanism is predicted by strain hardening exponent. For instance, when $n=2$ the main deformation mechanism is grain boundaries sliding. The degree of difficulty is predicted by activation energy of a material during hot working beneath certain deformation conditions.

According to the kinetic model, the steady-state flow stress can be interrelated to the temperature and strain rate over an Arrhenius equation during hot deformation (Jonas *et al.*, 1969):

$$\dot{\epsilon} = A\sigma^n e^{\frac{-Q}{RT}} \quad (1)$$

Where σ represent flow stress of materials; $\dot{\epsilon}$ signify strain rate; Q imply activation energy; A = a constant; n = stress exponent; T = temperature and R = gas constant (8.314 J/mol K).

Eq. (1) is effective for a wide range of processing parameters like temperature and strain rate for pure metals. In this case, the calculated activation energy is closely equal to the self-diffusion activation energy. However, for alloys and MMCs, Eq. (1) is effective on a narrow range of processing parameters and the estimated activation energy is exceeding than that for self-diffusion. This is due to the existence of second phase, solid solution or dispersion hardening in alloys and hard reinforcement in MMCs which often generate back stress during deformation. This complicates the evolution of rate-controlling deformation mechanisms in alloys and MMC materials. During hot deformation, the changes in the microstructure such as grain size, are usually interrelated through Zener-Hollomon parameter, Z , which is expressed as per Eq. (2) (Selvam *et al.*, 2015):

$$Z = \dot{\epsilon} e^{\frac{Q}{RT}} \quad (2)$$

In pure metals, the relation between average grain diameter and Z on a log scale is an inverse linear correlation. The limitation of the kinetic model is that it does not help in the microstructural control or optimization of the workability of commercial materials or the avoidance of defects in processing.

Atomistic Model-Raj Map

Atomistic model predicts the different mechanisms involved in the following three types of microstructural damage during hot working (Raj, 1981):

- (1) *Microstructural defect in the form of voids*: Conventional dimple type defects in ductile materials during deformation at moderate strain rate and low temperature which occurs due to void formation at the interface of hard particles and matrix;
- (2) *Wedge crack development*: Primary reason is due to grain boundary sliding action at grain boundary triple junctions, which dominates at higher temperatures and lower strain rates; and
- (3) *Adiabatic shear band creation*: Happens at very high strain rates and lower temperatures.

The equations used to stipulate the boundaries are obtained from suitable phenomenological and Raj models and the safe zones to prevent the above three damage causing processes (i.e., microstructural defect, wedge cracking, shear band creation) are established accordingly. Within this regime, excellent hot workability is obtained without causing any microstructure defects through the mechanism of dynamic recovery (DR) at lower temperatures and dynamic recrystallization (DRX) at higher temperature.

The validity of the Raj model is limited to dilute alloys and pure metals. However, for complex alloys and MMCs this model validity is undefined. In addition to this, different variety of experimental data are essential in order to plot the map. The different zone in the Raj map are dependent on the assumptions made concerning the microstructural properties. For instance, the cavitation domain zone would depend on the assumption of second phase particles and its distribution.

Dynamic Materials Modeling (DMM)-Processing Map

This model is based on the concepts of irreversible thermodynamics, modeling of physical systems, large scale study of plastic flow by continuum mechanics, deterministic disorder, and non-linear dynamics and hence it is extremely interdisciplinary (Rao and Prasad, 2014).

According to this model, the workpiece material dissipates power during high temperature deformation in two corresponding ways:

- (1) In the form of heat or temperature rise and
- (2) In the form of microstructural variation.

The hot workability of the specimen mainly depends on the power dissipation due to microstructural variation and should be evaluated explicitly. The dynamic constitutive equation used for hot workability/high-temperature deformation behavior of materials is as follows (Prasad *et al.*, 1984):

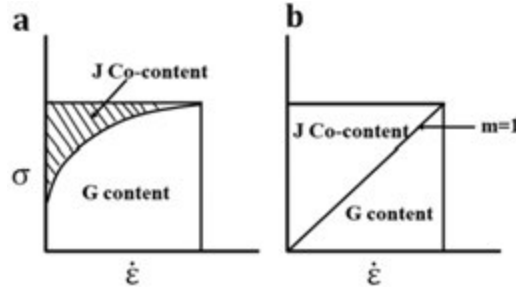


Fig. 3 Schematic figure of (a) G content and J co-content explanation and (b) $J_{\max}$ which occurs at $m = 1$.

$$\sigma = K\dot{\epsilon}^m \quad (3)$$

where σ represents stress, K is a constant, m stands for strain rate sensitivity, $\dot{\epsilon}$ represents applied strain rate.

Fig. 3(a) represents the schematic diagram for representing the constitutive equation which signifies the stress-strain rate behavior of a material obtained through the applied stress at a constant temperature and strain. At different applied strain rates, the path of the curve will be different. For instance, at lower strain rate, the material may experience a large plastic flow before failure and the material may undergo quick fracture with less plastic deformation at faster strain rates. The total power dissipated (P) is expressed as two corresponding functions given as (Prasad *et al.*, 1984):

$$P = \sigma \dot{\epsilon} \int_0^{\dot{\epsilon}} \sigma d\dot{\epsilon} + \int_0^{\sigma} \dot{\epsilon} d\sigma = G + J \quad (4)$$

The first integral function is termed as “G content” which indicates the key input power for plastic deformation and deformation heating. The second integral term is “J co-content” which represents the energy that microstructural changes dissipate.

The strain rate sensitivity (m) is found by means of differentiating the power between deformation heat and microstructural changes of flow stress.

$$\frac{dJ}{dG} = \frac{\partial P}{\partial G} \frac{\partial J}{\partial P} = \frac{\dot{\epsilon} d\sigma}{\sigma d\dot{\epsilon}} = \frac{\partial(\ln \sigma)}{\partial(\ln \dot{\epsilon})} = m \quad (5)$$

The J co-content can be obtained by substituting Eq. (3) in Eq. (4), we get:

$$J = \int_0^{\sigma} \dot{\epsilon} d\sigma = \frac{m}{m+1} \sigma \cdot \dot{\epsilon}^m \quad (6)$$

The J co-content value attains its maximum limit ($J_{\max}$) when strain rate sensitivity (m) = 1, and the workpiece acts as a linear dissipator; thus,

$$J_{\max} = \frac{\sigma \cdot \dot{\epsilon}}{2} \quad (7)$$

Fig. 3(b) representing schematic figure for stress-strain rate behavior of a material when $m = 1$. In this case, one-half of the power is exhausted by means of material flow and the other half is dissipated as heat.

The power dissipation efficiency (η) is obtained by considering ratio between power dissipated to the maximum power dissipation via microstructural revolution and is expressed as (Prasad *et al.*, 1984);

$$\eta = \frac{J}{J_{\max}} = \frac{m\sigma\dot{\epsilon}/m+1}{\sigma\dot{\epsilon}/2} = \frac{2m}{m+1} \quad (8)$$

Power dissipation and instability maps

The power dissipation or stability map is developed by using the values of power dissipation efficiencies (η) and plotted on $\log \dot{\epsilon}$ in Y-axis vs Temperature in X-axis. However, only partial information about the hot deformation is carried by the power dissipation map. The power dissipation map only gives information regarding the microstructure efficiency but unable to explain any instruction related to the instability of the hot deformation process. The instability maps describe the zone of instability and the unwanted deviations in the microstructural aspect (such as intergranular cracking, edge cracking etc.). These instability zones in the processing map are not safe and should be evaded during the hot deformation processing.

The criterion for instability is proposed by Prasad and Seshacharyulu. The criterion can be represented by the following relation when instability occurs (Prasad and Seshacharyulu, 1998):

$$\frac{\partial D}{\partial R} < \frac{D}{R} \quad (9)$$

where D represents dissipative function and R signifies the parameter related to strain rate. D can be replaced with J , the “co-content” in order to consider the microstructural dissipation, and the resultant equation for flow instability related by microstructure is expressed as per the following equation (Jonas *et al.*, 1969):

$$\xi(\dot{\epsilon}) = \frac{\partial \ln[m/(m+1)]}{\partial \ln \dot{\epsilon}} + m < 0 \quad (10)$$

The dimensionless parameter ξ can be calculated through Eq. (10) which is a function of deformation temperature and strain rate. The region with negative ξ values in processing map signifies flow instabilities. Flow instability microstructures demonstrate the presence of localized flow, adiabatic shear bands and wedge cracking (Son *et al.*, 2018).

Development of Processing Map

High precision experimental value on flow stress is required for the development of processing maps at different processing constraints such as strain rate and temperature. In order to construct processing maps, the processing parameters have to be selected by considering real life manufacturing simulations for hot workability such as: the preferred temperature ranges (generally from 0.65 to 0.85 T/T_m) and the range of strain rate (usually varies from 0.0003 to 100 s^{-1}).

The following requirements/assumptions are often made while developing the processing maps as per this modeling approach:

- (1) A constant true strain rate is preferred than nominal strain rate,
- (2) The temperature distribution should be uniform throughout the test material, and
- (3) The rise in temperature during deformation should be measured to get the actual flow stress.

For achieving the constant true strain, isothermal hot compression testing is a suitable process. A standard cylindrical specimen with L/D ratio in the range of 1.2–1.5 is generally used to conduct compression tests. In order to maintain the isothermal conditions, the platens, push-pull rods and specimens have to be heated together inside the furnace. While deforming at ambient temperatures, (1) appropriate lubricant (such as graphite, MoS₂, or molten glass) should be used to reduce friction between the specimen and the holder and (2) applied deformation strain (true strain) should be within the threshold range (~ 0.7 – 1.0%) to avoid barrelling effect. After compression testing, the elastic portion should be subtracted from load vs. stroke length data for the machine compliance correction and then these data should be transformed into true stress-true strain curves as per the following equations (Zhong *et al.*, 2014):

$$\text{True stress } (\dot{\sigma}) = \frac{F}{A_0(1 - \epsilon)} \quad (11)$$

$$\text{True strain } (\dot{\epsilon}) = \ln(l_0 - l) \quad (12)$$

Where F represents the load applied during deformation, ϵ signifies engineering strain, A_0 indicates original area of cross-section of the sample, l_0 = original height of the sample and l = instantaneous height.

Similarly, the flow stress information at various strain levels are obtained at different range of three process parameters such as strain rates, strains and temperatures. There may be increase in temperature at high strain rates (above 1 s^{-1}). It is required to incorporate the suitable correction factors in the flow stress values at such strain rate level of loading conditions. The corrected flow stress versus temperature and strain rate are generally being used as input to generate processing maps at various strain levels.

The first step for obtaining a processing map is to calculate strain rate sensitivity (m). For this, the log (flow stress) vs log (strain rate) curve is drawn and then fitted by using a spline function. The value of m is dependent on strain rate and is calculated at distinct processing temperatures. Then the efficiency of power dissipation (η) is estimated as per Eq. (8). The obtained η value is a function of deformation strain rate and temperature and is used to draw the contour map in temperature vs log (strain rate) frame, that establishes the power dissipation map (Fig. 4(a)). The instability map is plotted using m values that help to determine the instability parameters (Eq. (8)) (Fig. 4(b)). The boundaries for power dissipation map and instabilities are superimposed to obtain the processing map (Fig. 4(c)).

Mechanisms of Processing Map for Metal Matrix Composites

The processing map for MMC material consists of different zones namely stable or safe and instable or unsafe zone. The deformation mechanisms responsible for safe and unsafe zones in different MMCs are explained in this section.

Stable Zone

The stable zone of a processing map signifies the safe workability region of material without the formation of any defect. In this zone, the deformation mechanism is mainly dominated by dynamic recovery (DR), dynamic recrystallization (DRX), and super plasticity (Rao and Prasad, 2014). However, the occurrence of DRX is more efficient than that of DR during hot deformation as DRX provides softening along with microstructural reconstruction.

Dynamic recrystallization (DRX)

In this process, recrystallized grains are simultaneously formed during deformation by both nucleation and growth processes. In MMC materials, the presence of hard reinforcement plays a significant role in nucleation and growth of these DRX grains more

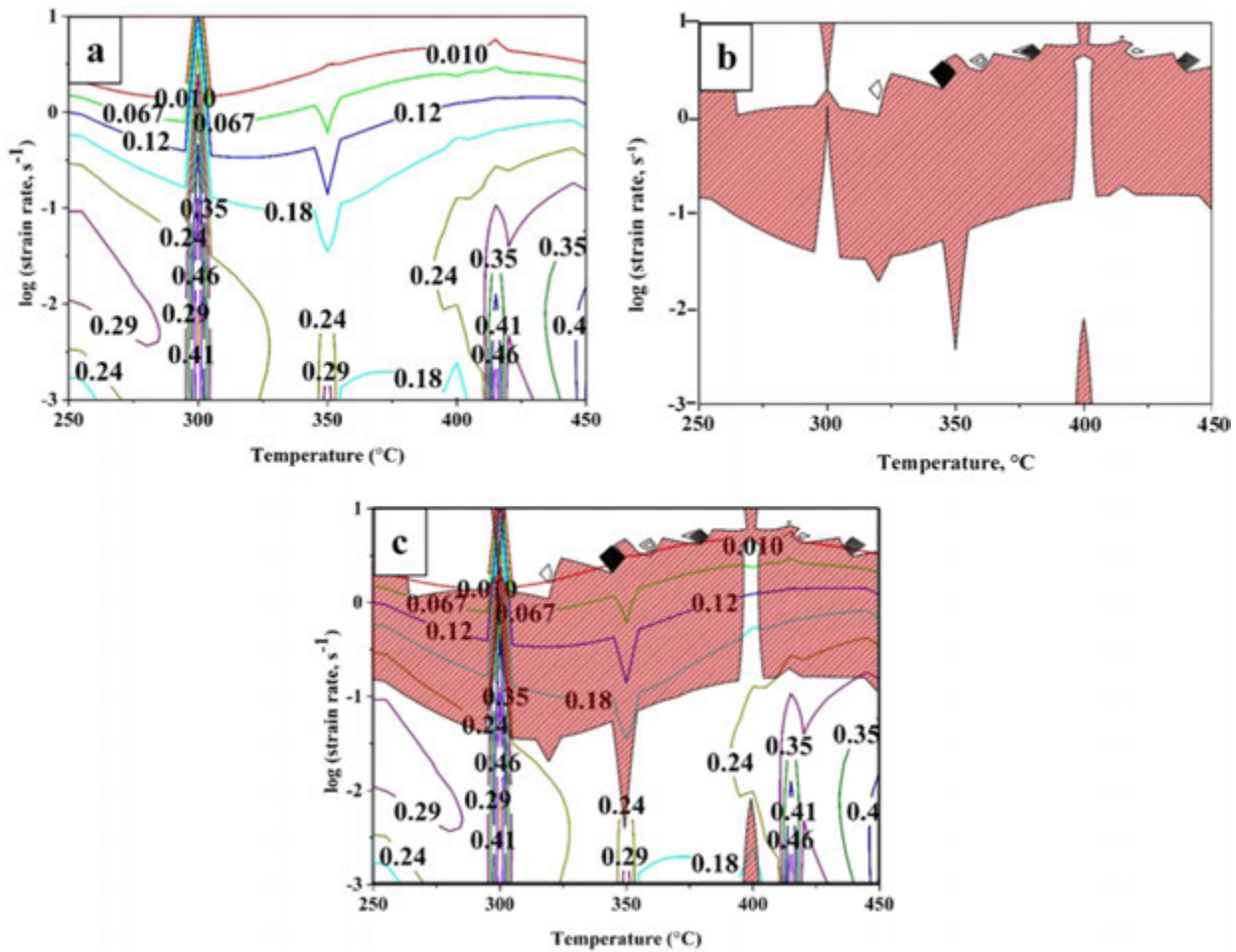


Fig. 4 Schematic diagram for (a) power dissipation map (b) instability map and (c) processing map.

prominently than unreinforced alloys. The tendency for occurrence of DR and DRX can also be observed indirectly by flow stress response (decrease in flow stress indicates the existence of DR and DRX) and directly by detailed microstructural characterization (EBSD, TEM, SEM, Optical, etc).

The processes of DRX can be described in two ways (a) continuous DRX and (b) discontinuous DRX. In continuous DRX, the nucleation of new grains form homogeneously all over the materials and the growth of these grains are rare. In contrast, discontinuous DRX involves both nucleation and irregular growth of new grains. Continuous DRX can be termed as a single-step deformation process whereas discontinuous DRX is known as double-step process.

The misorientation of grain boundary is also a key factor for DRX nucleation. The dislocations get accumulated at the vicinity of grain boundaries and form substructures near them. Further, the formed substructure is engrossed by dislocations near it and progressively shielded by low angle grain boundaries (LAGBs). When there is a transformation of LAGBs to high angle grain boundaries (HAGBs), re-crystallized grains nucleate. This propensity of the recrystallization method is identified as continuous DRX.

Fig. 5 shows the EBSD micrograph of a stable zone for a solution treated AZ91 magnesium alloy (base) and AZ91/TiC + TiB₂ (composite) magnesium matrix in-situ composite (Sahoo and Panigrahi, 2019a). The microstructure consists of two types of DRX grains (1) partially developed discontinuous DRX grains (**Fig. 5(a)**) in the base material and (2) a full-grown equiaxed continuous DRX grains (**Fig. 5(b)**) in the composite material. The difference in morphology of DRX grains is due to variation in dislocation generation as there is an existence of coefficient of thermal expansion (CTE) discrepancy between matrix and in-situ reinforcement. Further, these dislocation motions are hindered by in-situ reinforcement during deformation which caused a supplementary pile-up of dislocations in the material. Because of this, more activation energy is required for occurrence of DRX in the composite material as compared to the base material. The fraction of LGBs are found to be 10.3% and 8.7% for base and composite material respectively (**Fig. 5**). Therefore, composite material contains more continuous DRXs grains as compared to the base material.

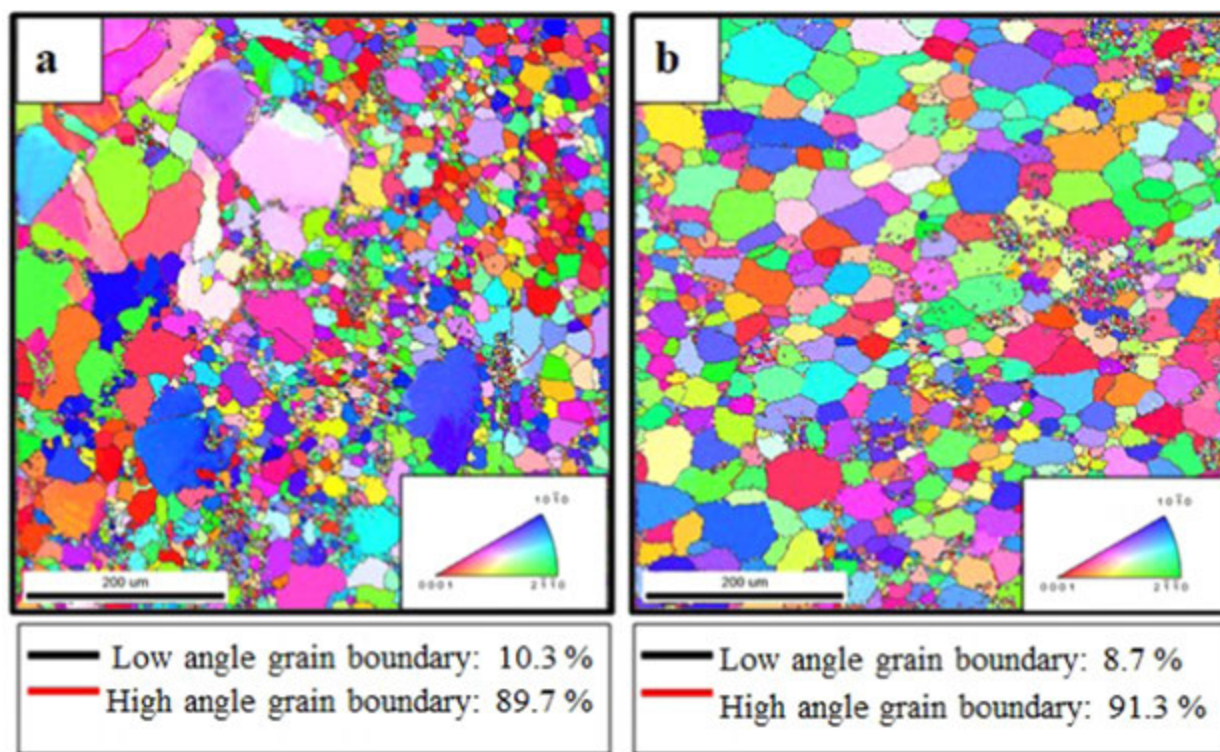


Fig. 5 EBSD microstructure of stable zone for (a) AZ91 alloy and (b) AZ91 + (TiC + TiB₂) in-situ composite. Reproduced from Sahoo, B.N., Panigrahi, S.K., 2019a. Deformation behavior and processing map development of AZ91 Mg alloy with and without addition of hybrid in-situ TiC + TiB₂ reinforcement. *J. Alloy. Compd.* 776, 865–882. doi:10.1016/j.jallcom.2018.10.276 with permission from Elsevier.

Dynamic recovery (DR)

Besides DRX, the other deformation mechanism in stable zone is dynamic recovery which usually happens at lower strain rates and temperatures. This domain is observed in the hot working of materials where workability is usually limited compared to that in DRX domain. This mechanism also relies on the SFE of the material and occurs mainly on high SFE materials such as aluminum.

One such DR dominated microstructure of a hot deformed MMCs (ZK60 Mg matrix reinforced with Al₁₈B₄O₃₃ and 2024 Al matrix reinforced with ZrB₂) are shown in Fig. 6. The presence of low dislocation density and more fraction of subgrains are the signature of DR dominated microstructure. Further, these sub grain boundaries formed due to DR is gradually transformed into new high angle grain boundaries at large strains (Wang *et al.*, 2008).

Superplastic deformation

The 3rd mechanism that occurs during stable zone deformation is super-plasticity. This domain pops up at a low strain rate and high temperature, where the dominant mechanism is the viscous process of grain boundary sliding. Grain boundary sliding mechanism generally occurs in materials with smaller and equiaxed grains (< 10 μm). The superplastic domain is not a completely “safe” zone except during deformation processing the state of stress is controlled. There is a high chance for cavitation and wedge-cracking during superplastic deformation.

Instable Zone

The different mechanisms responsible in the instability zone of processing map is wedge cracking, localized plastic flow and adiabatic shear bands.

Wedge cracking

Wedge cracking mainly appears when the deformation temperatures are high and strain rates are low (Ramanathan *et al.*, 2006). At such deformation domain (high temperature and low strain rate), superplastic deformation via grain boundary sliding is dominant. Because of the presence of grain boundary sliding, stress concentration arises at the triple junctions of grain boundary. If this stress concentration is not relieved by the strain accommodation process quickly, then wedge cracking occurs.

Fig. 7 represents the SEM microstructure of Al6063 + (Al₂O₃ + Y₂O₃) nano-composite which exhibited wedge cracking during deformation at T = 400°C and $\dot{\epsilon}$ = 0.1 s⁻¹.

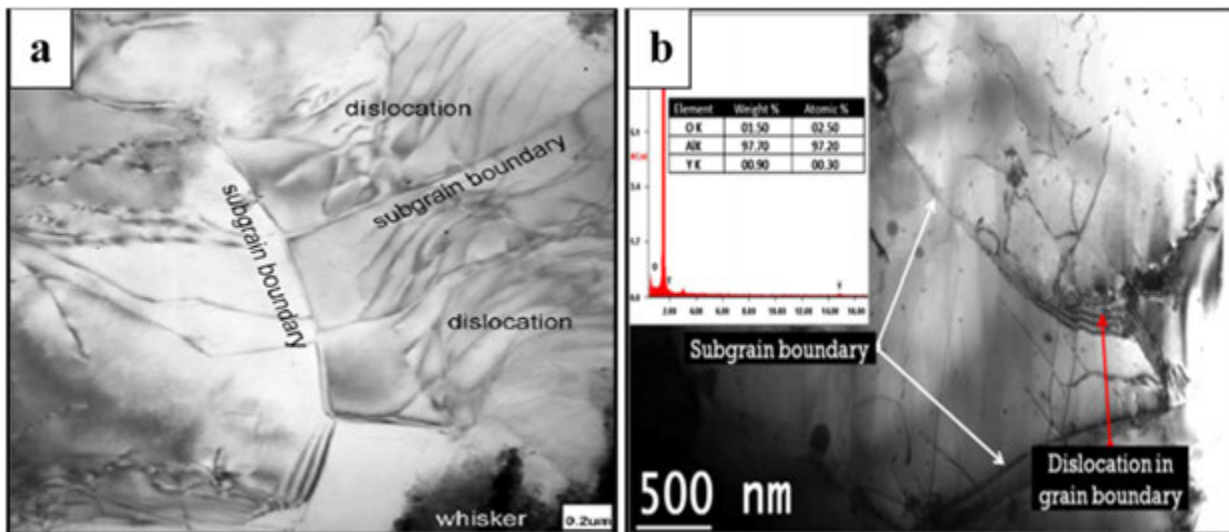


Fig. 6 TEM microstructure showing dynamic recovery of (a) ZK60 + Al₁₈B₄O₃₃ composite deformed at $T = 623\text{K}$ and $\dot{\epsilon} = 0.01\text{ s}^{-1}$. (b) Al2024 + ZrB₂ deformed at $T = 300^\circ\text{C}$ and $\dot{\epsilon} = 0.001\text{ s}^{-1}$. Reproduced from (a) Wang, C.Y., Wu, K., Zheng, M.Y., 2008. Hot deformation and processing maps of Al₁₈B₄O₃₃/ZK60 composite. *Mater. Sci. Eng. A* 477, 179–184. doi:10.1016/j.msea.2007.06.023. (b) Kai, X., Zhao, Y., Wang, A., Wang, C., Mao, Z., 2015. Hot deformation behavior of in situ nano ZrB₂ reinforced 2024Al matrix composite. *Compos. Sci. Technol.* 116, 1–8. doi:10.1016/j.compscitech.2015.05.006 with permission from Elsevier.

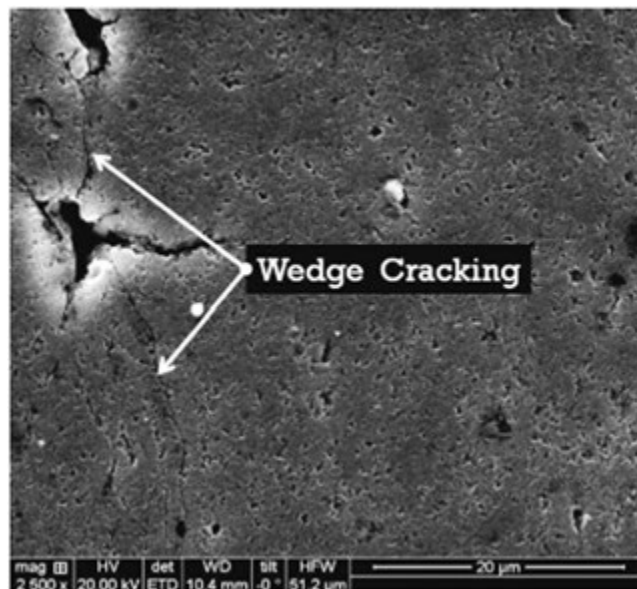


Fig. 7 SEM micrograph displaying wedge cracking at $T = 400^\circ\text{C}$ and $\dot{\epsilon} = 0.01\text{ s}^{-1}$. Reproduced from Ahamed, H., Senthilkumar, V., 2012. Hot deformation behavior of mechanically alloyed Al6063/0.75Al₂O₃/0.75Y₂O₃ nano-composite – A study using constitutive modeling and processing map. *Mater. Sci. Eng. A* 539, 349–359. doi:10.1016/j.msea.2012.01.109 with permission from Elsevier.

In addition to wedge cracking, the deformation mechanism in instability zone comprise formation of void at hard particles (ductile fracture), inter-crystalline cracking or hot shortness (at high temperatures and high strain rates value), and cracking along the prior particle boundaries (only in the case of P/M billets). Along with these mechanisms, the microstructure characteristic can also be hampered through deformation because of the formation of flow instabilities, which is illustrated in different ways such as: flow localization, dynamic strain aging, adiabatic shear band development and flow rotation.

When a MMC deforms at low temperature and high strain rate, the presence of hard particles in the soft matrix results in large accumulated stresses due to gradient in plasticity between matrix and reinforcement, which leads to crack and debonding at the matrix-reinforcement interface along with microstructural damage because of cavity formation. This results in poor ductility and

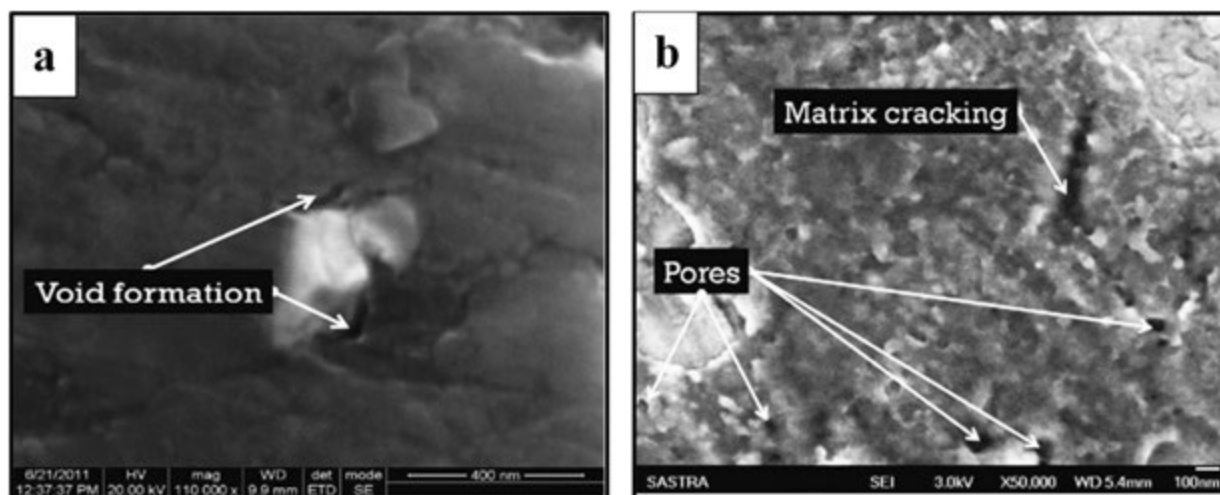


Fig. 8 SEM micrograph showing (a) void formation at $T = 350^{\circ}\text{C}$ and $\dot{\epsilon} = 0.1 \text{ s}^{-1}$, and (b) matrix cracking and pores at $T = 500^{\circ}\text{C}$ and $\dot{\epsilon} = 0.1 \text{ s}^{-1}$ in the nano-composite. Reproduced from Ahamed, H., Senthilkumar, V., 2012. Hot deformation behavior of mechanically alloyed $\text{Al6063}/0.75\text{Al}_2\text{O}_3/0.75\text{Y}_2\text{O}_3$ nano-composite – A study using constitutive modeling and processing map. *Mater. Sci. Eng. A.* 539, 349–359. doi:10.1016/j.msea.2012.01.109 with permission from Elsevier.

inferior workability of MMCs. **Fig. 8(a)** represents SEM micrograph of nano Al MMC material deformed at $T = 350^{\circ}\text{C}$ and $\dot{\epsilon} = 0.1 \text{ s}^{-1}$ which represents void formation in the nano-composite.

Deformation at high temperature and high strain rate in MMCs develop cracks and pores in the matrix and matrix/reinforcement interface. At high temperatures, the matrix of MMC becomes soft. When the soft matrix undergoes high strain rate deformation, flow stress suddenly increases due to the lack of deformation time and particle reinforcement mismatch. When the local flow stress exceeds the fracture stress, crack initiates mainly at the particle/matrix interphase followed by crack growth upon further loading. Hence, this region in processing map is not appropriate for bulk metal processing and this should be avoided. **Fig. 8(b)** represents similar kind of microstructure which shows cracks and pores deformed at $T = 500^{\circ}\text{C}$ and $\dot{\epsilon} = 0.1 \text{ s}^{-1}$ of nano Al MMC material.

Network structure in MMC also plays a significant role in deciding the workability of materials. **Fig. 9** shows network structured TiBw particle reinforced Ti6Al4V composites with instable deformation features. The debonding between the hard TiB particles and a soft matrix is observed in the network boundary (**Fig. 9(a)**). This is due to the inconsistent deformation between the reinforcement (TiBw particles) – matrix interface at a high strain rate (10 s^{-1}). Also, the presence of flow localization bands can be observed in **Fig. 9(b)** which represents excessively elongated α grains in the compressed matrix zone. The presence of the flow localization bands is due to the low thermal conductivity of Ti6Al4V matrix. Furthermore, the presence of network structure in MMC is possibly detrimental to heat conduction at high strain rates.

Processing Map of Metal Matrix Composite

The MMCs contain different types of both reinforcements and matrices which influence their hot deformation behavior and hence significantly influence their processing maps. Several researchers have developed processing maps for (1) Al-based MMCs, (2) Mg-based MMCs and (3) Ti-based MMCs. They established the mechanisms behind the difference of the workability of these MMCs as compared to unreinforced counterpart alloy.

Aluminum Metal Matrix Composite

Aluminum metal matrix composites (AMMCs) are extensively used in the aerospace and automobile industry for their lightweight, high specific stiffness, strength to weight ratio, good formability and high-temperature resistance (Jaseem *et al.*, 2018). Being Al as matrix material, the crystal structure of AMMCs is FCC which has 12 number of slip systems. In order to have proper deformation, at least 5 independent slip systems are essential. Due to sufficient number of slip systems, AMMCs show a reasonable ductility with combination of strength at room temperature. During hot deformation processing, these AMMCs are affected by different processing parameters such as strain rates and temperatures. Many researchers have been investigating the safe workability limit of these developed AMMCs by processing maps.

Addition of reinforcement makes a reasonable improvement in hot workability limit of Al alloys. **Fig. 10** shows the comparison of processing map for Al 7075 alloy (Rajamuthamilselvan and Ramanathan, 2011) and Al 7075 + SiC composite (Rajamuthamilselvan *et al.*, 2010). The optimum workability limits for base alloy is at temperature and strain rate of 350°C and 0.1 s^{-1}

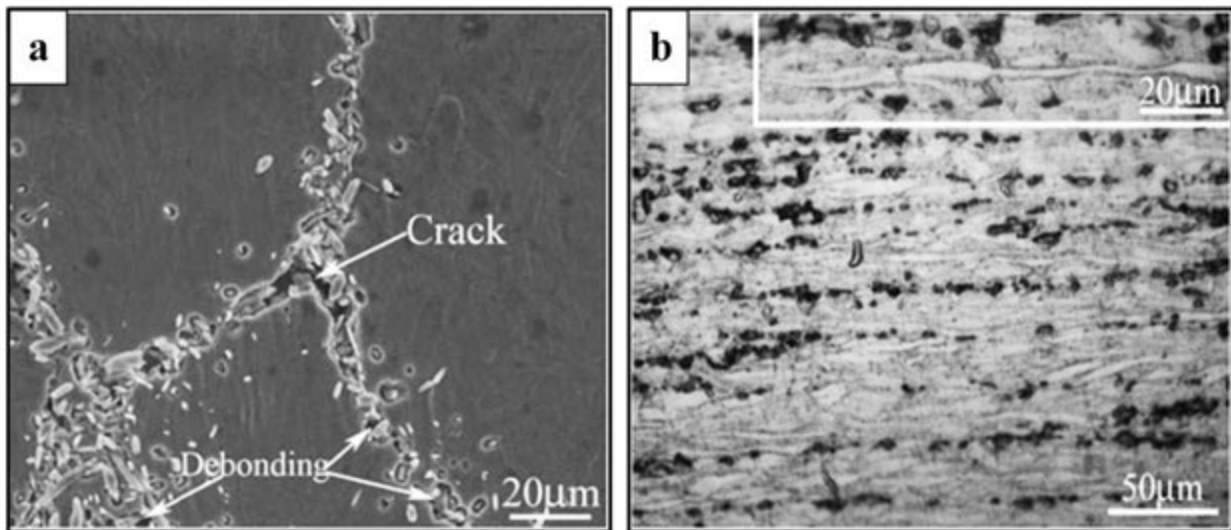


Fig. 9 (a) SEM and (b) microstructure of network structure TiBw/Ti6Al4V composite. Reproduced from Huang, L.J., Zhang, Y.Z., Geng, L., Wang, B., Ren, W., 2013. Hot compression characteristics of TiBw/Ti6Al4V composites with novel network microstructure using processing maps. *Mater. Sci. Eng. A* 580, 242–249. doi:10.1016/j.msea.2013.05.039 with permission from Elsevier.

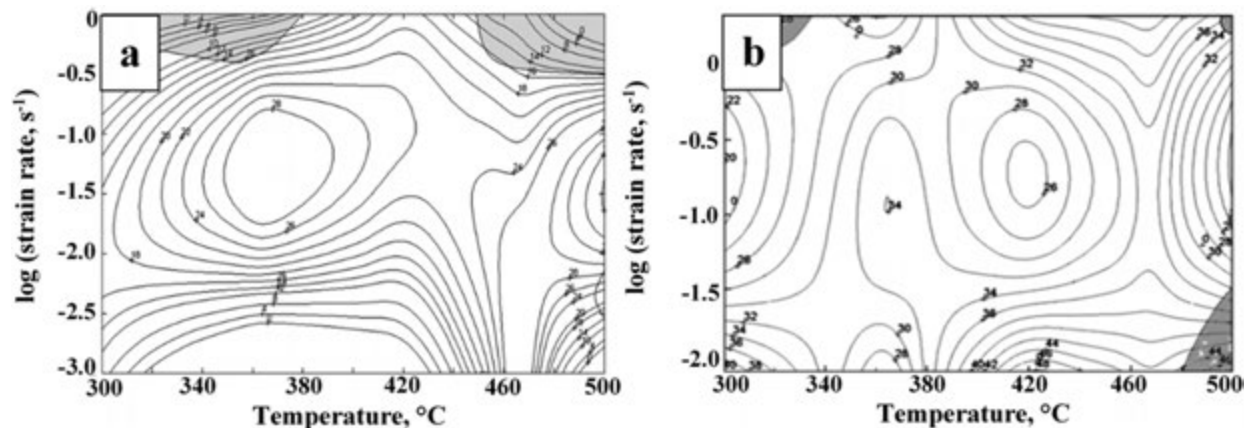


Fig. 10 Processing map of (a) Al 7075 alloy and (b) Al 7075 + SiC composite at a strain of 0.5. Reproduced from Rajamuthamilselan, M., Ramanathan, S., 2011. Hot deformation behavior of 7075 alloy. *J. Alloy. Compd.* 509, 948–952. doi:10.1016/j.jallcom.2010.09.139. Rajamuthamilselan, M., Ramanathan, S., Karthikeyan, R., 2010. Processing map for hot working of SiCp/7075 Al composites. *Trans. Nonferr. Met. Soc. China* 20, 668–674. doi:10.1016/S1003-6326(09)60196-5 with permission from Elsevier.

respectively with power dissipation efficiency (η) of 28%. The workability range of its composite has increased to temperature range of about 380–440°C and strain rate range of 0.1–0.9 s⁻¹ with the η value varies from 26%–30%.

According to Fig. 10, the deformation temperature for workability domain of Al 7075-SiC composite has increased by about 50°C as compared to its unreinforced counterpart with a comparative reduction in the flow instability regime. The improvement in workability temperature is basically due to presence of SiC particles which provides a back stress during deformation.

The deformation strain has also influenced the processing map of AMMCs. Fig. 11 demonstrates the processing maps for Al2024 + ZrB₂ composite at different strains of 0.2, 0.4, 0.6 and 0.8 (Kai *et al.*, 2015). The stable zone area of processing map, is represented by green color shadow and that of instable zone is marked in red color shadow. The power dissipation efficiency (η) value is found to be less than 30% for strain of 0.2 and 0.4, whereas η value is greater than 30% at strain of 0.6 and 0.8. The instability region also increases with increase in strain. Table 1 represents the optimum workability conditions for processing map of different AMMCs.

From Table 1 it can be seen that the optimum conditions for workability of AMMCs depend on size, volume fraction and types of reinforcement. Most of the processing maps comprise of two stable zones. The processing parameters for 1st stable zone varies from 350 to 440°C and at a strain rate of 0.001–0.1 s⁻¹. The 2nd stable zone occurs at higher temperatures varying from 440 to 475°C and strain rate of 0.03–1.0 s⁻¹. The deformation mechanism of stable zone is same as discussed in Section “Stable Zone”

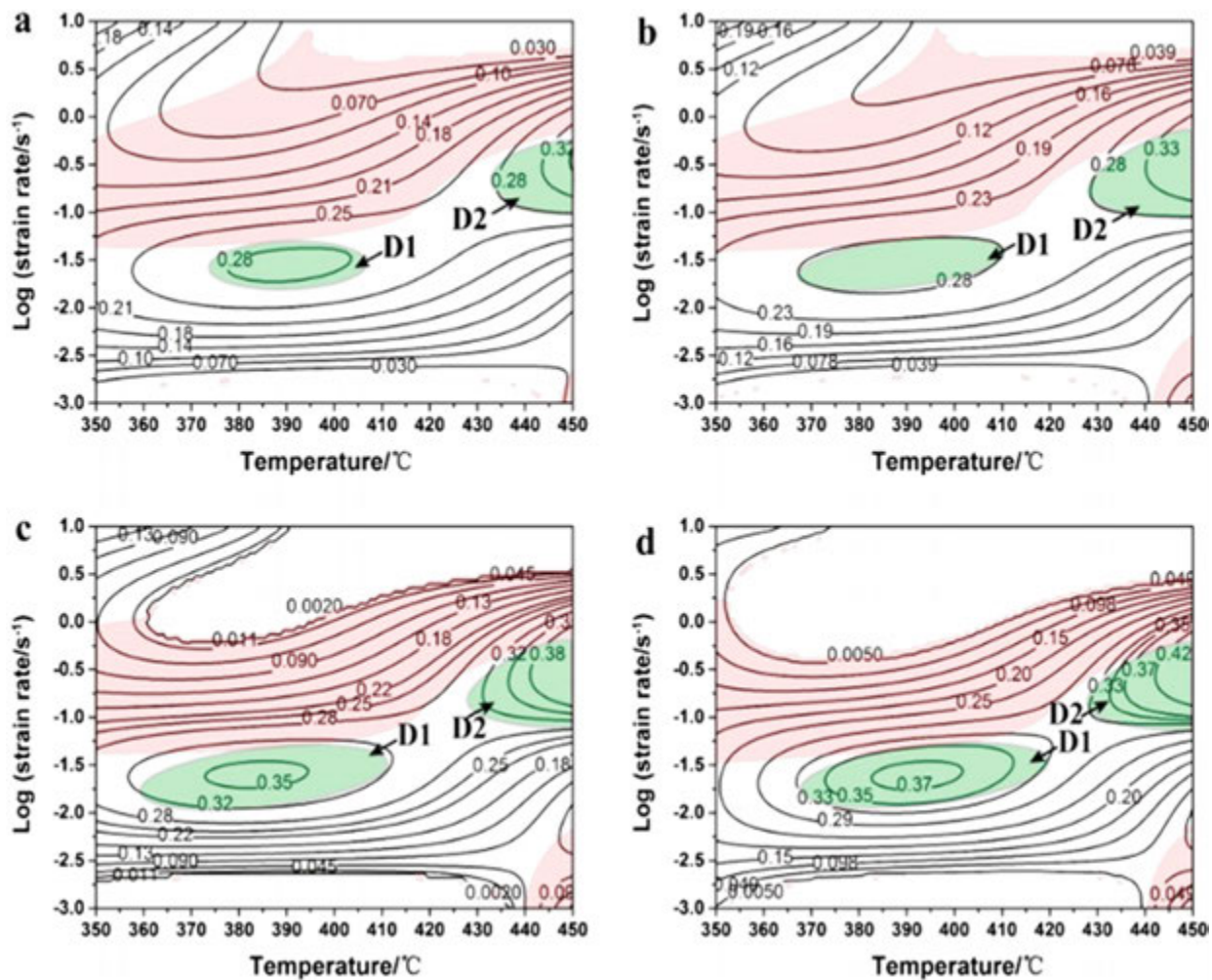


Fig. 11 Processing maps for Al2024 + ZrB₂ composite at strain of (a) 0.2, (b) 0.4, (c) 0.6 and (d) 0.8. Reproduced from Kai, X., Zhao, Y., Wang, A., Wang, C., Mao, Z., 2015. Hot deformation behavior of in situ nano ZrB₂ reinforced 2024Al matrix composite. *Compos. Sci. Technol.* 116, 1–8. doi:10.1016/j.compscitech.2015.05.006 with permission from Elsevier.

Table 1 Optimum processing conditions for aluminum metal matrix composite

Sl. no.	Material (Matrix + reinforcement)	Process parameters (temperature range and strain rate range)	Optimum conditions (temperature range/ strain rate range)	References
01	Al 6061 + 10 vol% SiC	300–500°C, 0.001–1 s ⁻¹	450–500°C & 0.1–1 s ⁻¹	Li <i>et al.</i> (2016)
02	Al 2024 + 5 wt% nano ZrB ₂	350–450°C, 0.001–10 s ⁻¹	Zone I: 380–410°C & 0.018–0.032 s ⁻¹ Zone II: 440–460°C & 0.075–0.56 s ⁻¹	Kai <i>et al.</i> (2015)
03	Al 6063 + (0.75Al ₂ O ₃ + 0.75Y ₂ O ₃)	300–500°C, 0.001–1 s ⁻¹	Zone I: 395–440°C & 0.001–0.01 s ⁻¹ Zone II: 440–500°C & 0.003–0.01 s ⁻¹	Ahamed and Senthilkumar (2012)
04	Al alloy + Al ₂ O ₃	360–480°C, 0.001–1 s ⁻¹	Zone I: 360–400°C & 0.001–0.01 s ⁻¹ Zone II: 400–440°C & 0.001–1 s ⁻¹	Yang <i>et al.</i> (2012)
05	Al 2024 + 20 vol% SiCP	400–475°C, 0.001–1.0 s ⁻¹	Zone I: 400–430°C & 0.001–0.003 s ⁻¹ Zone II: 440–475°C & 0.03–1.0 s ⁻¹	Shao <i>et al.</i> (2010)
06	Al 2124 + 15% SiC	300–500°C, 0.001–1.0 s ⁻¹	Zone I: 360–460°C, & 0.01–0.56 s ⁻¹ Zone II: 460–500°C, & 0.001–0.002 s ⁻¹	Ramanathan <i>et al.</i> (2006)
07	Al 2618 + Al ₂ O ₃	350–500°C, 10 ⁻¹ –10 ⁻³ s ⁻¹	450°C & 0.03 s ⁻¹	Cavaliere <i>et al.</i> (2004)
08	Al 6061 + 20% Al ₂ O ₃	350–500°C, 10 ⁻¹ –10 ⁻³ s ⁻¹	500°C & 0.07 s ⁻¹	Cerri <i>et al.</i> (2002)

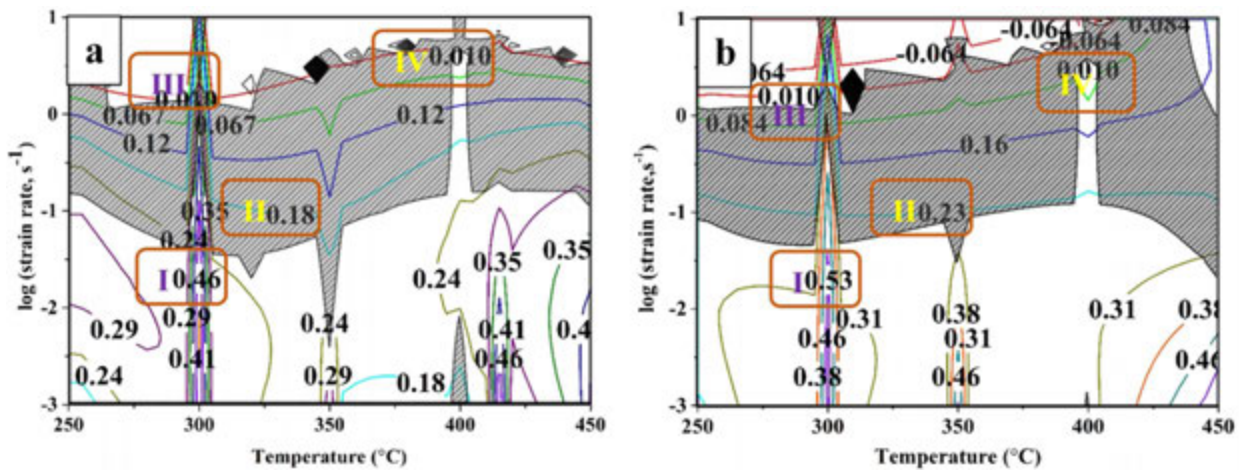


Fig. 12 Processing map of AZ91 Mg alloy and (b) AZ91/(TiC + TiB₂) Mg in-situ composite at a strain of 0.5. Reproduced from Sahoo, B.N., Panigrahi, S.K., 2019a. Deformation behavior and processing map development of AZ91 Mg alloy with and without addition of hybrid in-situ TiC + TiB₂ reinforcement. *J. Alloy. Compd.* 776, 865–882. doi:10.1016/j.jallcom.2018.10.276 with permission from Elsevier.

i.e., it consists of DR, DRX and superplastic deformation mechanism. Al being a high stacking fault energy material, the deformation mechanism at elevated temperature is DR. As the 1st stable zone is at low temperature and high strain rate, DR is main softening mechanism in this zone (Fig. 6(b)). Deformation in zone 2 (i.e., at high temperature and low strain rate) leads to mostly dynamic recovery in matrix and dynamic recrystallization at particle or reinforcement/matrix interface. At higher temperatures and slow strain rates, the fraction of low angle grain boundaries (LAGBs) (49.4%) were reduced drastically and high angle grain boundaries (HAGBs) (50.6%) were increased. In this zone, the LAGBs were rearranged due to the dynamic recovery and transferred into the HAGBs. Due to this transformation of LAGBs to HAGBs, DRX mostly occurs during deformation.

Magnesium Matrix Metal Matrix Composite

Magnesium metal matrix composites (MMMCs) have fascinated widespread attention for their promising applications in aerospace, automotive and defense industries due to their low density, high specific strength and stiffness (Sahoo and Panigrahi, 2019b, 2018b; Sahoo et al., 2018; Sahoo and Panigrahi, 2018a). However, the addition of hard brittle ceramic particles and hexagonal closed packed crystal structure of magnesium matrix limits their plastic deformability at room and low temperatures. Therefore, the MMCs are generally deformed at high temperatures in order to activate additional slip systems during deformation.

Addition of reinforcement makes additional improvement in deformation behavior at elevated temperature of Mg alloys. Fig. 12 shows the comparison between processing map of AZ91 Mg base alloy and AZ91/(TiC + TiB₂) Mg in-situ composite (Sahoo and Panigrahi, 2019a). Due to presence of in-situ TiC + TiB₂ reinforcement, the power dissipation efficiency (η) increases from 0.46 (base alloy) to 0.53 (in-situ composite).

The processing map of MMCs is also sensitive to strain. Fig. 13 demonstrates the processing maps for AZ91 + bimodal size SiC composite at different strains of 0.3, 0.4 and 0.5 (Zhou et al., 2014). In the processing map, the stable zone area is larger at strain 0.3 as compared to other strains (i.e., at strain 0.4 and 0.5). The power dissipation efficiency (η) value of stable zone at strain 0.3 is also found to be higher than other strain conditions. The η value in stable zone at strain 0.3 is found to be 44%, which appears in the lower strain rate and at the temperature range of 370–420°C (Fig. 13(a)). However, in the case of higher strains of 0.4 and 0.5 (Fig. 13(b) and (c)), the η value appears at temperature range of 270–370°C. In addition, the power dissipation efficiency (η) value increases with increasing strain from 0.3 to 0.5 at lower temperature range (270–370°C) whereas at high temperature range (370–420°C) the value of η decreases with increasing strain. The instability region also increases with increase in strain.

The size of reinforcement also plays an important role in deciding the workability limit of processing map. Fig. 14 represents the comparison between stable zone and instable zone of AZ91 alloy, micro-SiC + AZ91 composite and nano-SiC + AZ91 composite. From the figure, it can be concluded that the stable zone area of nanocomposite is broad as compared to micro-composite and base alloy (Fig. 14(a)). The instability zone comparison of the three materials is represented in Fig. 14(b) and there is no instability zone for AZ91 alloy as it appears at a comparatively high strain rate ($> 1.0 \text{ s}^{-1}$), which is beyond the range shown. The presence of micron and nano-size SiC particles extend the area of the instability zone of the matrix to a lower strain rate and even higher temperature.

Table 2 represents optimum parameters for processing map on Mg MMC.

From the Table 2 it can be seen that the optimum processing condition for obtaining best workability of most of the MMCs are mostly having three zones (Zone-I, Zone-II and Zone III). The temperature range in Zone-I, Zone-II and Zone-III mostly varies

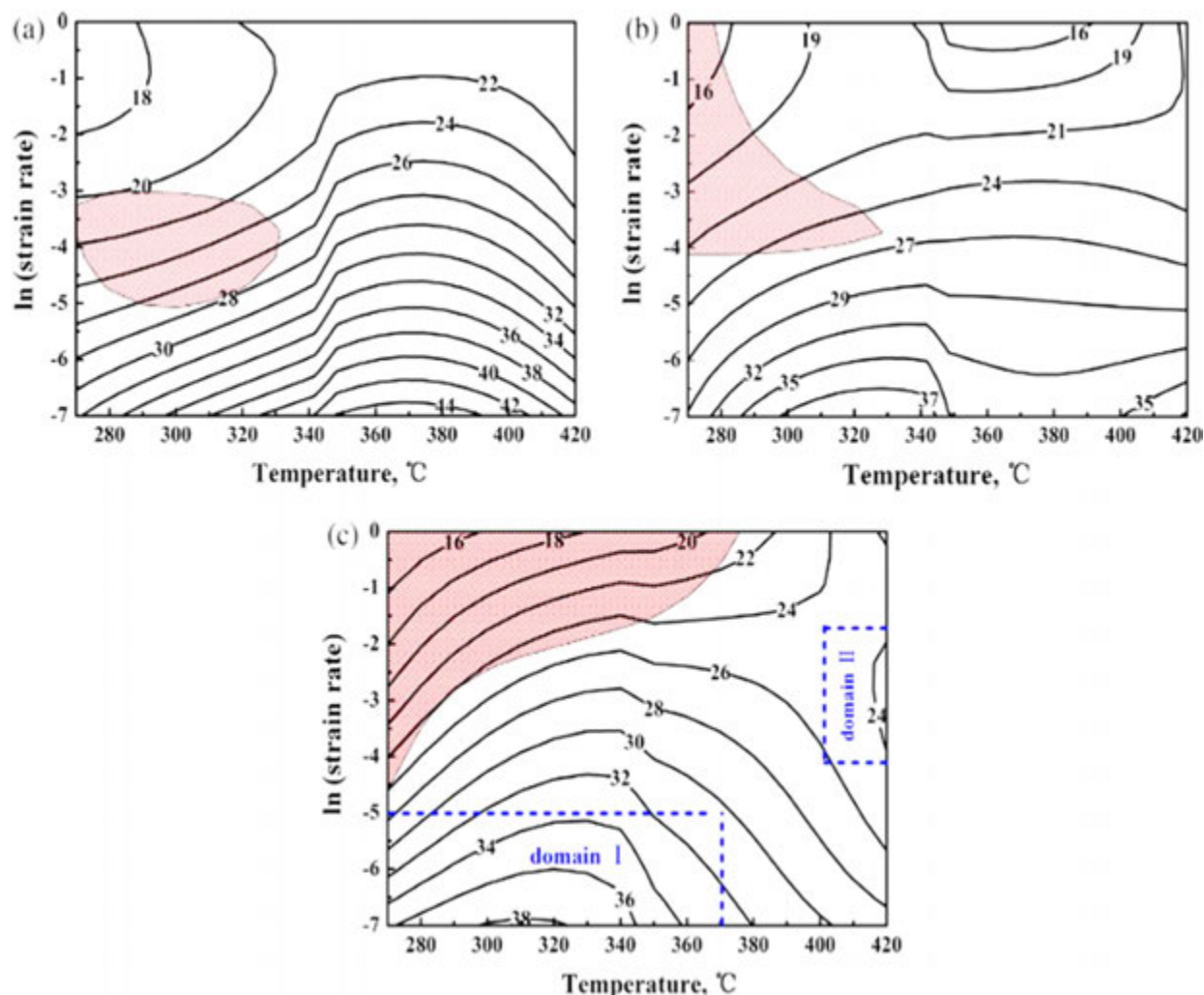


Fig. 13 Processing maps of the AZ91 + SiC composite at the strains of (a) 0.3, (b) 0.4 and (c) 0.5. Reproduced from Zhou, S.S., Deng, K.K., Li, J.C., *et al.*, 2014. Hot deformation behavior and workability characteristics of bimodal size SiCp/AZ91 magnesium matrix composite with processing map. *Mater. Des.* 64, 177–184. doi:10.1016/j.matdes.2014.07.039 with permission from Elsevier.

in the temperature range of 250–350 $^{\circ}\text{C}$, 350–410 $^{\circ}\text{C}$ and 410–490 $^{\circ}\text{C}$ respectively. In order to understand the influence of different temperature on hot deformation mechanism of MMCs, it is important to understand the different deformation mode in Mg alloy/MMCs. There are four possible deformation occurs in Mg and its alloys (Panigrahi *et al.*, 2011): (1) basal slip, i.e., slip on the (0001) plane with a $\langle 11\bar{2}0 \rangle$ Burgers vector, (2) prismatic slip ($10\bar{1}0$) $\langle 11\bar{2}0 \rangle$, (3) first-order pyramidal slip type ($10\bar{1}1$) $\langle 11\bar{2}0 \rangle$ and (4) second-order pyramidal slip ($c + a$) type-II ($211\bar{2}$) $\langle \bar{2}113 \rangle$. Activation of these slip systems depend on their CRSS value. The CRSS of above-mentioned four slip systems are in the ratio of 1:30:50:100 at room temperature. Basal slip and prismatic slip get activated during deformation at room temperature and low temperature respectively where as second order pyramidal slip system get activated above 400 $^{\circ}\text{C}$.

Magnesium is a high stacking fault energy (SFE) material, alike to those of aluminum (Ion *et al.*, 1982) and therefore, during high temperature deformation, MMCs might be expected to soften by dynamic recovery rather than dynamic recrystallization. However, most of the stable zone in MMCs shows the presence of dynamic recrystallization during the deformation at high temperature (Fig. 5). This is due to the deficiency of slip systems in magnesium rather than to the effect of SFE. As the 1st stable zone is at low temperature, basal slip is the easiest mode to activate during deformation. However, there are only two independent slip systems in basal slip, which still does not provide the five independent slip systems which is essential for homogeneous deformation of a polycrystalline material. To fulfill this condition, an additional twin system is activated during low temperature deformation. The temperature in Zone II and III is favorable for activation $c + a$ dislocation of the second-order pyramidal system. Also, cross-slip occurs in pyramidal slip systems that significantly contribute to the restoration of the DRX nucleus. Since many pyramid systems are involved, the nucleation rate will be faster than the grain boundary displacement. DRX will therefore be controlled by migration rates, depending on the self-diffusion.

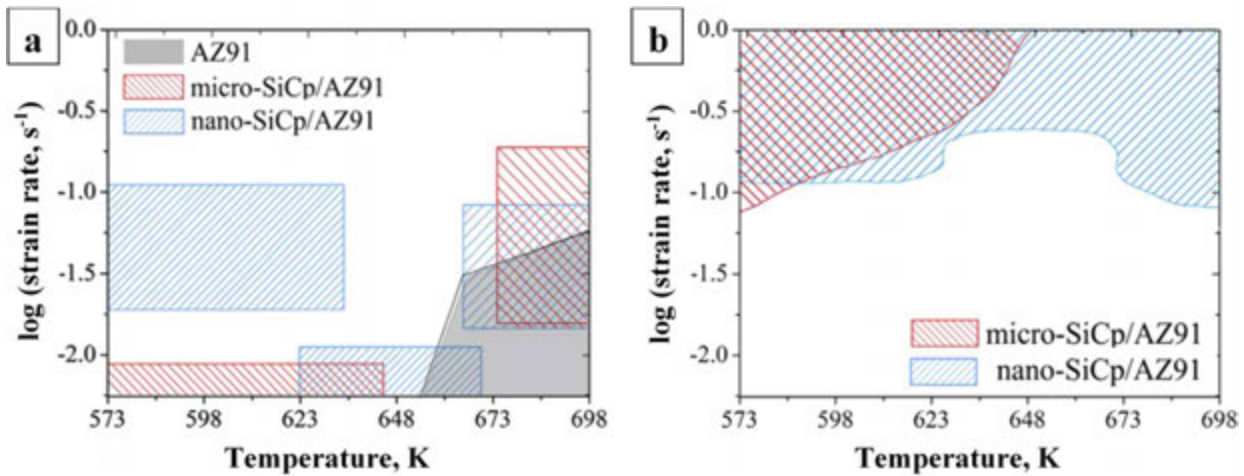


Fig. 14 Comparisons among AZ91 alloy, micro-SiCp/AZ91 composites and nano-SiCp/AZ91 composites in terms of their (a) workability domains and (b) instability domains. Reproduced from Mu, M., Zhi-Min, Z., Bao-Hong, Z., Jin, D., 2012. Flow behaviors and processing maps of as-cast and as-homogenized AZ91 alloy. *J. Alloy. Compd.* 513, 112–117. doi:10.1016/j.jallcom.2011.09.102. Zhou, S.S., Deng, K.K., Li, J.C., *et al.*, 2014. Hot deformation behavior and workability characteristics of bimodal size SiCp/AZ91 magnesium matrix composite with processing map. *Mater. Des.* 64, 177–184. doi:10.1016/j.matdes.2014.07.039. Zhang, L., Wang, Q., Liu, G., *et al.*, 2017. Effect of SiC particles and the particulate size on the hot deformation and processing map of AZ91 magnesium matrix composites. *Mater. Sci. Eng. A.* 707, 315–324. doi:10.1016/j.msea.2017.09.056 with permission from Elsevier.

Table 2 Optimum processing conditions for magnesium metal matrix composite

Sl. no.	Material (Matrix + reinforcement)	Process parameters (temperature range and strain rate range)	Optimum conditions (temperature range/strain rate range)	References
01	AZ91 + (TiC + TiB ₂)	250–500°C, 0.001–10 s ⁻¹	300°C & 0.01 s ⁻¹	Sahoo and Panigrahi, 2019a Zhang <i>et al.</i> (2017)
02	AZ91 + SiC	300–425°C, 0.005–1 s ⁻¹	Zone I: 300–362°C & 0.02–0.1 s ⁻¹ Zone II: 350–400°C & 0.005–0.012 s ⁻¹ Zone III: 395–425°C & 0.016–0.1 s ⁻¹	
03	AZ91 + SiC	250–400°C, 0.001 s ⁻¹ to 1 s ⁻¹	400°C & 0.001 s ⁻¹	Wang <i>et al.</i> (2016)
04	AZ31 + (1Ca + 1.5 vol% Al ₂ O ₃)	250–500°C, 0.0003–10 s ⁻¹	Zone I: 250–350°C & 0.0003–0.01 s ⁻¹ Zone II: 350–410°C & 0.0003–0.01 s ⁻¹ Zone III: 410–490°C & 0.002–0.2 s ⁻¹	Suresh <i>et al.</i> (2015)
05	Mg + ZnO	250–400°C, 0.01–1.5 s ⁻¹	375–400°C & 0.01 s ⁻¹	Selvam <i>et al.</i> (2015)
06	AZ91 + SiC	270–420°C, 0.001 s ⁻¹ to 1 s ⁻¹	270–250°C & 0.001–0.1 s ⁻¹	Deng <i>et al.</i> (2015)
07	AZ91 + SiC	270–420°C, 0.001–1 s ⁻¹	Zone I: 270–370°C & 0.001–0.01 s ⁻¹ Zone II: 420°C & 0.01 s ⁻¹	Zhou <i>et al.</i> (2014)
08	AZ31B + (1.5% (vol%) Al ₂ O ₃ + 1% Ca)	250–400°C, 0.01–1.0 s ⁻¹	400°C & 0.01 s ⁻¹	Srinivasan <i>et al.</i> (2013)
09	AZ91 + TiC	250–400°C, 0.001–10 s ⁻¹	300°C & 0.001 s ⁻¹	Liu <i>et al.</i> (2010a)
10	Mg + Al ₂ O ₃	300–500°C, 0.0003–10 s ⁻¹	400–450°C & >0.1 s ⁻¹	Prasad <i>et al.</i> (2009)
11	AZ91 + Ti	300–500°C, 0.001–1 s ⁻¹	420–500°C & 0.01–0.1 s ⁻¹	Raghunath <i>et al.</i> (2008)
12	ZK60 + Al ₁₈ B ₄ O ₃₃ W	250–450°C, 0.001–10 s ⁻¹	400°C & 0.1 s ⁻¹	Wang <i>et al.</i> (2008)

Titanium Matrix Metal Matrix Composite

Ti alloys exhibit high specific strength, excellent high-temperature strength which make them potential candidate for variety of structural components in aerospace, high temperature appliances and medical sectors. The addition of ceramic reinforcement can further enhance mechanical properties of Ti alloys. Few researchers have studied the high-temperature behavior of titanium matrix metal matrix composites (TMMCs) through processing map and established their deformation mechanisms.

The addition of ceramic reinforcement to Ti alloy affects the stable zone of processing map. Fig. 15 represents the processing map for Ti–1.5Fe–2.25Mo–0.6Y alloy and Ti–1.5Fe–2.25Mo–0.6Y + 10% Mo₂C composite (Liu *et al.*, 2010b). The area under stable zone is found to be more in alloy as compared to composite. This is due to large difference in elastic modulus between matrix and reinforcement which resulted void formation during deformation in composite. Table 3 represents the processing map details of the published literature on TMMCs.

As per Table 3, the optimum processing condition for obtaining best workability of most of the TMMCs are generally varying between 900–980°C. This optimum workability range (900–980°C) of TMMCs is higher than that of AMMC and MMC materials. The crystal

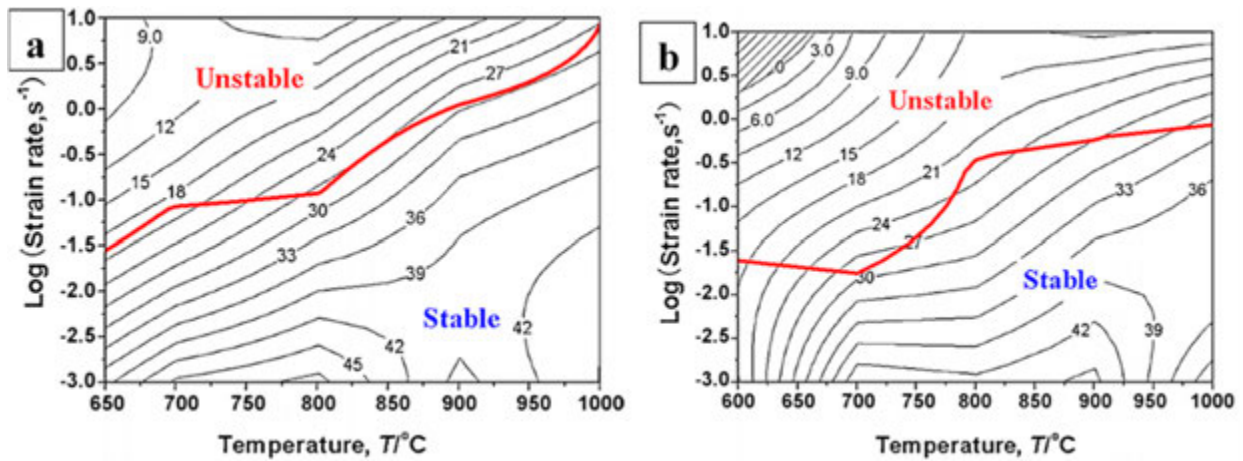


Fig. 15 Processing map of (a) Ti-1.5Fe-2.25Mo-0.6Y alloy and (b) Ti-1.5Fe-2.25Mo-0.6Y + 10% Mo₂C composite. Reproduced from Liu, B., Li, Y.P., Matsumoto, H., *et al.*, 2010b. Thermomechanical response of particulate-reinforced powder metallurgy titanium matrix composites – A study using processing map. *Mater. Sci. Eng. A*. 527, 4733–4741. doi:10.1016/j.msea.2010.04.003 with permission from Elsevier.

Table 3 Optimum processing conditions for titanium metal matrix composite

Sl. no.	Material (Matrix+ reinforcement)	Process parameter (temperature range and strain rate range)	Optimum conditions (temperature range/strain rate range)	References
01	Ti-6Al-4V + TiB	900–1200°C, 0.001–10 s ⁻¹	900°C & 0.001 s ⁻¹	Xu <i>et al.</i> (2018a)
02	Ti6Al4V + TiBw	900–1100°C, 0.001–10 s ⁻¹	920–980°C & 0.01–0.1 s ⁻¹	Huang <i>et al.</i> (2013)
03	Ti-1.5Fe-2.25Mo-0.6Y + 10% Mo ₂ C	600–1000°C, 0.001–10 s ⁻¹	700–900°C & 10 ⁻³ –10 ⁻² s ⁻¹	Liu <i>et al.</i> (2010b)
04	Ti-6Al-6V-2Sn + 12 vol% of TiC	650–950°C, 0.015–15 s ⁻¹	800–950°C & 0.1 s ⁻¹	Poletti <i>et al.</i> (2008)

structure of Ti alloy at room temperature and pressure is hexagonal close-packed (HCP) α phase through a c/a ratio of 1.587. The Ti alloy experiences an allotropic conversion to a body-centered cubic (BCC) β phase at about 890°C, which remains stable up to the melting temperature. Due to BCC crystal structure, it is easy to deform the Ti alloy in this zone as compared to α phase which is HCP structure. Therefore, all the stable zone falls in the range of 900–980°C. The number of literatures on high-temperature behavior study of TMMCs is comparatively lesser than AMMCs and MMMCs due to difficulty in processing of TMMCs at high temperature domain.

Conclusion

The hot workability of metal matrix composites (MMCs) necessitates a systematic understanding of their constitutive behavior during hot working deformation domain. This is usually done by modeling the MMCs during hot working deformation behavior with objectives of establishing the conditions for optimal workability safe processing domain and for evading micro and macro defects in the material. Though kinetic and atomistic models have been developed over the years, the more appropriate and recent model for MMCs is based on illustrating the dynamic material behavior by means of processing maps.

The processing map of MMCs establishes their safe/stable and unsafe/instable hot working processing zones. The main deformation mechanism for stable zone is dynamic recrystallization (DRX), dynamic recovery (DR) and superplasticity. Whereas, wedge cracking, pores, cavitation are the dominant deformation mechanisms in instable zones.

In aluminum metal matrix composite (AMMC) both DR and DRX are the primary deformation mechanisms of the stable zone. Since aluminum is having high stacking fault energy (SFE), the deformation mechanism is DR based at low temperature and DRX based at high temperature. This is due to transformation of low angle grain boundaries to high angle grain boundaries during deformation at high temperature.

In magnesium metal matrix composite (MMMC), deformation occurs through DRX. At high temperature many pyramid systems are involved during deformation and hence the nucleation rate will be faster than the grain boundary displacement. DRX will therefore be controlled by migration rates, depending on the self-diffusion of MMMCs.

The stable zone in titanium metal matrix composite (TMMCs) falls in the range of 900–980°C. This is due to the Ti alloy experiences an allotropic conversion to a body-centered cubic (BCC) β phase at about 890°C, which remains stable up to the melting temperature. Due to BCC crystal structure, it is easy to deform the Ti alloy in this zone as compared to α phase which is HCP structure.

In conclusion, the processing map technique has proven to be an influential tool to expose the optimum conditions for hot workability domain by appraise process parameters and to accomplish microstructural control in the MMCs material.

References

- Ahamed, H., Senthilkumar, V., 2012. Hot deformation behavior of mechanically alloyed $\text{Al6063}/0.75\text{Al}_2\text{O}_3/0.75\text{Y}_2\text{O}_3$ nano-composite – A study using constitutive modeling and processing map. *Mater. Sci. Eng. A* 539, 349–359. doi:10.1016/j.msea.2012.01.109.
- Cavaliere, P., Cerri, E., Leo, P., 2004. Hot deformation and processing maps of a particulate reinforced $2618/\text{Al}_2\text{O}_3/20\text{p}$ metal matrix composite. *Compos. Sci. Technol.* 64, 1287–1291. doi:10.1016/j.compscitech.2003.10.007.
- Cerri, E., Spigarelli, S., Evangelista, E., Cavaliere, P., 2002. Hot deformation and processing maps of a particulate-reinforced 6061 + 20% Al_2O_3 composite. *Mater. Sci. Eng. A* 324, 157–161. doi:10.1016/S0921-5093(01)01299-0.
- Deng, K., Li, J., Xu, F., Nie, K., Liang, W., 2015. Hot deformation behavior and processing maps of fine-grained $\text{SiCp}/\text{AZ91}$ composite. *Mater. Des.* 67, 72–81.
- Huang, L.J., Zhang, Y.Z., Geng, L., Wang, B., Ren, W., 2013. Hot compression characteristics of $\text{TiBw}/\text{Ti6Al4V}$ composites with novel network microstructure using processing maps. *Mater. Sci. Eng. A* 580, 242–249. doi:10.1016/0001-6160(82)90031-1.
- Ion, S.E., Humphreys, F.J., White, S.H., 1982. Dynamic recrystallisation and the development of microstructure during the high temperature deformation of magnesium. *Acta Metall.* 30, 1909–1919. doi:10.1016/0001-6160(82)90031-1.
- Jaseem, I., Immanuel, R.J., Rao, P.N., *et al.*, 2018. Synergetic effect of cryorolling and post-roll aging on simultaneous increase in wear resistance and mechanical properties of an Al-Cu alloy. *J. Tribol.* 140, 1–11. doi:10.1115/1.4040162.
- Jonas, J.J., Sellars, C.M., Tegart, W.J.M.G., 1969. Strength and structure under hot-working conditions. *Metall. Rev.* 14, 1–24. doi:10.1179/mtrl.1969.14.1.1.
- Kai, X., Zhao, Y., Wang, A., Wang, C., Mao, Z., 2015. Hot deformation behavior of in situ nano ZrB_2 reinforced 2024Al matrix composite. *Compos. Sci. Technol.* 116, 1–8. doi:10.1016/j.compscitech.2015.05.006.
- Langdon, T.G., Mohamed, F.A., 1978. A simple method of constructing an Ashby-type deformation mechanism map. *J. Mater. Sci.* 13, 1282–1290. doi:10.1007/BF00544735.
- Li, X.P., Liu, C.Y., Sun, X.W., Ma, M.Z., Liu, R.P., 2016. Hot deformation behaviour and processing maps of AA6061-10 vol% SiC composite prepared by spark plasma sintering. *Sci. China Technol. Sci.* 59, 980–988. doi:10.1007/s11431-016-6063-9.
- Liu, B., Li, Y.P., Matsumoto, H., *et al.*, 2010b. Thermomechanical response of particulate-reinforced powder metallurgy titanium matrix composites – A study using processing map. *Mater. Sci. Eng. A* 527, 4733–4741. doi:10.1016/j.msea.2010.04.003.
- Liu, R., Cao, W., Fan, T., Zhang, C., Zhang, D., 2010a. Development of processing maps for 3vol% $\text{TiCp}/\text{AZ91D}$ composites material. *Mater. Sci. Eng. A* 527, 4687–4693. doi:10.1016/j.msea.2010.03.095.
- Liu, R., Wang, B., Li, J., Ma, W., Hu, S., 2019. Deformation behavior and microstructure evolution of powder metallurgy Ti6Al4V alloy during hot compression. *J. Mater. Eng. Perform.* 28, 4454–4466. doi:10.1007/s11665-019-04166-0.
- Mokdad, F., Chen, D.L., Liu, Z.Y., *et al.*, 2017. Hot deformation and activation energy of a CNT-reinforced aluminum matrix nanocomposite. *Mater. Sci. Eng. A* 695, 322–331. doi:10.1016/j.msea.2017.04.006.
- Panigrahi, S.K., Yuan, W., Mishra, R.S., *et al.*, 2011. A study on the combined effect of forging and aging in Mg-Y-RE alloy. *Mater. Sci. Eng. A* 530, 28–35. doi:10.1016/j.msea.2011.08.065.
- Poletti, C., Degischer, H.P., Kremmer, S., Marketz, W., 2008. Processing maps of Ti662 unreinforced and reinforced with TiC particles according to dynamic models. *Mater. Sci. Eng. A* 486, 127–137. doi:10.1016/j.msea.2007.08.077.
- Prasad, Y.V.R.K., Seshacharyulu, T., 1998. Processing maps for hot working of titanium alloys. *Mater. Sci. Eng. A* 243, 82–88. doi:10.1016/S0921-5093(97)00782-X.
- Prasad, Y.V.R.K., Rao, K.P., Gupta, M., 2009. Hot workability and deformation mechanisms in Mg/nano- Al_2O_3 composite. *Compos. Sci. Technol.* 69, 1070–1076. doi:10.1016/j.compscitech.2009.01.032.
- Prasad, Y.V.R.K., Geggel, H.L., Doraivelu, S.M., *et al.*, 1984. Modeling of dynamic material behavior in hot deformation: forging of Ti-6242. *Metall. Trans. A* 15, 1883–1892. doi:10.1007/BF02664902.
- Raghunath, B.K., Karthikeyan, R., Ganesan, G., Gupta, M., 2008. An investigation of hot deformation response of particulate-reinforced magnesium + 9% titanium composite. *Mater. Des.* 29, 622–627. doi:10.1016/j.matdes.2007.02.012.
- Raj, R., 1981. Development of a processing map for use in warm-forming and hot-forming processes. *Metall. Trans. A* 12, 1089–1097. doi:10.1007/BF02643490.
- Rajamuthamilselvan, M., Ramanathan, S., 2011. Hot deformation behaviour of 7075 alloy. *J. Alloy. Compd.* 509, 948–952. doi:10.1016/j.jallcom.2010.09.139.
- Rajamuthamilselvan, M., Ramanathan, S., Karthikeyan, R., 2010. Processing map for hot working of $\text{SiCp}/7075$ Al composites. *Trans. Nonferr. Met. Soc. China* 20, 668–674. doi:10.1016/S1003-6326(09)60196-5.
- Ramanathan, S., Karthikeyan, R., Ganaseen, G., 2006. Development of processing maps for 2124Al/SiCp composites. *Mater. Sci. Eng. A* 441, 321–325. doi:10.1016/j.msea.2006.08.044.
- Rao, K.P., Prasad, Y.V.R.K., 2014. Advanced Techniques to Evaluate Hot Workability of Materials. Elsevier. doi:10.1016/B978-0-08-096532-1.00321-6.
- Sahoo, B.N., Panigrahi, S.K., 2018a. A study on the combined effect of in-situ (TiC-TiB_2) reinforcement and aging treatment on the yield asymmetry of magnesium matrix composite. *J. Alloy. Compd.* 737, 575–589. doi:10.1016/j.jallcom.2017.12.027.
- Sahoo, B.N., Panigrahi, S.K., 2018b. Effect of in-situ (TiC-TiB_2) reinforcement on aging and mechanical behavior of AZ91 magnesium matrix composite. *Mater. Charact.* 139, 221–232. doi:10.1016/j.matchar.2018.03.002.
- Sahoo, B.N., Panigrahi, S.K., 2019a. Deformation behavior and processing map development of AZ91 Mg alloy with and without addition of hybrid in-situ $\text{TiC} + \text{TiB}_2$ reinforcement. *J. Alloy. Compd.* 776, 865–882. doi:10.1016/j.jallcom.2018.10.276.
- Sahoo, B.N., Panigrahi, S.K., 2019b. Development of wear maps of in-situ $\text{TiC} + \text{TiB}_2$ reinforced AZ91 Mg matrix composite with varying microstructural conditions. *Tribol. Int.* 463–477. doi:10.1016/j.triboint.2019.02.029.
- Sahoo, B.N., MD, F.K., Babu, S., Panigrahi, S.K., Ram, G.D.J., 2018. Microstructural modification and its effect on strengthening mechanism and yield asymmetry of in-situ $\text{TiC-TiB}_2/\text{AZ91}$ magnesium matrix composite. *Mater. Sci. Eng. A* 724, 269–282. doi:10.1016/j.msea.2018.03.060.
- Selvam, B., Marimuthu, P., Narayanasamy, R., *et al.*, 2015. Effect of temperature and strain rate on compressive response of extruded magnesium nano-composite. *J. Magnes. Alloy* 3, 224–230. doi:10.1016/j.jma.2015.07.002.
- Shao, J.C., Xiao, B.L., Wang, Q.Z., *et al.*, 2010. Constitutive flow behavior and hot workability of powder metallurgy processed 20 vol% $\text{SiCp}/2024\text{Al}$ composite. *Mater. Sci. Eng. A* 527, 7865–7872. doi:10.1016/j.msea.2010.08.080.
- Son, K.T., Kim, M.H., Kim, S.W., Lee, J.W., Hyun, S.K., 2018. Evaluation of hot deformation characteristics in modified AA5052 using processing map and activation energy map under deformation heating. *J. Alloy. Compd.* 740, 96–108. doi:10.1016/j.jallcom.2017.12.357.
- Srinivasan, M., Loganathan, C., Narayanasamy, R., *et al.*, 2013. Study on hot deformation behavior and microstructure evolution of cast-extruded AZ31B magnesium alloy and nanocomposite using processing map. *Mater. Des.* 47, 449–455. doi:10.1016/j.matdes.2012.11.028.
- Suresh, K., Dharmendra, C., Rao, K.P., Prasad, Y.V.R.K., Gupta, M., 2015. Processing map of AZ31-1Ca-1.5 vol% nano-alumina composite for hot working. *Mater. Manuf. Process.* 30, 1161–1167. doi:10.1080/10426914.2015.1025966.

- Wang, C.Y., Wu, K., Zheng, M.Y., 2008. Hot deformation and processing maps of $\text{Al}_{18}\text{B}_4\text{O}_{33}\text{w/ZK60}$ composite. *Mater. Sci. Eng. A* 477, 179–184. doi:10.1016/j.msea.2007.06.023.
- Wang, T., Nie, K.B., Deng, K.K., Liang, W., 2016. Analysis of hot deformation behavior and microstructure evolution of as-cast SiC nanoparticles reinforced magnesium matrix composite. *J. Mater. Res.* 31, 3437–3447. doi:10.1557/jmr.2016.362.
- Xu, R., Liu, B., Liu, Y., *et al.*, 2018a. High temperature deformation behavior of in-situ synthesized titanium-based composite reinforced with ultra-fine TiB whiskers. *Materials* 11, 1–13. doi:10.3390/ma11101863.
- Xu, W., Jin, X., Xiong, W., Zeng, X., Shan, D., 2018b. Study on hot deformation behavior and workability of squeeze-cast 20 vol% SiCw/6061Al composites using processing map. *Mater. Charact.* 135, 154–166. doi:10.1016/j.matchar.2017.11.026.
- Yang, Y., Zhang, Z., Zhang, X., 2012. Processing map of Al_2O_3 particulate reinforced Al alloy matrix composites. *Mater. Sci. Eng. A* 558, 112–118. doi:10.1016/j.msea.2012.07.092.
- Zang, Q., Yu, H., Lee, Y.S., Kim, M.S., Kim, H.W., 2019. Effects of initial microstructure on hot deformation behavior of Al-7.9Zn-2.7Mg-2.0Cu (wt%) alloy. *Mater. Charact.* 151, 404–413. doi:10.1016/j.matchar.2019.03.019.
- Zhang, L., Wang, Q., Liu, G., *et al.*, 2017. Effect of SiC particles and the particulate size on the hot deformation and processing map of AZ91 magnesium matrix composites. *Mater. Sci. Eng. A* 707, 315–324. doi:10.1016/j.msea.2017.09.056.
- Zhong, T., Rao, K.P., Prasad, Y.V.R.K., Zhao, F., Gupta, M., 2014. Hot deformation mechanisms, microstructure and texture evolution in extruded AZ31–nano-alumina composite. *Mater. Sci. Eng. A* 589, 41–49. doi:10.1016/j.msea.2013.09.062.
- Zhou, S.S., Deng, K.K., Li, J.C., *et al.*, 2014. Hot deformation behavior and workability characteristics of bimodal size SiCp/AZ91 magnesium matrix composite with processing map. *Mater. Des.* 64, 177–184. doi:10.1016/j.matdes.2014.07.039.

Microstructural Aspects of Metal-Matrix Composites

Devadas Bhat Panemangalore, Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar, Karnataka, India

Rajashekhar Shabadi, Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207-UMET-Unité Matériaux et Transformations, F-59000 Lille, France

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composites consist of two parts, a matrix which is a metal and the embedded reinforcement could be an organic constituent, ceramic, metallic or any other material. The properties of composite materials are tailored such that it is greater than the properties of the individual materials. For the past few decades this has been a major source of interest for many scientific researchers, which finds applications in aerospace, automobiles, sporting goods etc. Several journal articles and proceedings have been published depicting the advanced applications of these materials by developing their machining, electronic, tribological, physical, mechanical, optical properties, etc. Due to the unlimited possibilities in designing these composites by combining various materials, they could possibly replace several conventional materials in the near future.

In principle, any two or more materials can be combined to form a composite (Ashby, 2001). Composites can be synthesized using a number of material classes like metals, ceramics, glasses, elastomers and polymers (Ashby, 2001). Understanding these materials requires fundamental knowledge of its structure, property, processing and performance – the concept of materials science tetrahedron. Their microstructures are different as compared to metals and alloys, due to the interaction between different constituents (e.g., metal-ceramic) and the presence of interfaces.

Generalities About the Composites

Depending on the type of matrix (organic, metallic and ceramic), the first basis of classification is the binder, which is generally a soft phase. Organic can be classified into polymer-based and carbon-carbon type. Fiber reinforced glasses (FRG) and intermetallic compound matrix composites (IMC) are other classifications of composites (Bauri *et al.*, 2018).

Types and characteristics of MMCs

Staab (1999) classified MMCs into three categories depending on their solubility and interaction between the matrix and reinforcements. Al_2O_3 in Cu MMCs (Rajkovic *et al.*, 2014) belonged to Class I type (Staab, 1999) where there is no interaction between these constituents as they are insoluble. Partial solubility and interaction over a period of time is observed for W/Cu type MMCs, which was categorized to Class II (Staab, 1999). SiC in Al MMCs (Basak *et al.*, 2019) was categorized to Class III type where manufacturing issues take place that can be treated via optimum control in processing (Staab, 1999). In general, MMCs have high thermal conductivity (Qu *et al.*, 2011), electrical conductivity (Zuo *et al.*, 2020), strength (Russell *et al.*, 1999), fracture toughness (Mileiko *et al.*, 2020), wear resistance as compared to other materials. Several Al, Ti, Ni and Cu based MMCs are used for high performance applications (Pandey *et al.*, 2010). Addition of boron nitride to Cu based MMCs was studied by Chen *et al.* (2020b) to enhance the tribological behavior of brake-pad/disc friction pairs in high-speed trains. Shabadi *et al.* (2015) studied the thermal conductivity behavior of yttria reinforced copper. Friction stir processing was used to synthesize these composites for functional applications and with yttria addition, the coefficient of thermal expansion reduced due to a modified microstructure.

Materials

Matrix

The matrix in MMCs can be either a metal or an alloy. Among MMCs, several types exist, most commonly aluminum, magnesium, copper, nickel, nickel aluminides and titanium. Aluminum based MMCs are typically used to manufacture brake parts and engine pistons. Magnesium based MMCs are used today for biomedical applications (Bommala *et al.*, 2019). Al and Mg MMCs are the most commonly used matrices for requirements such as specific strength. With respect to its microstructure, factors such as residual stress, chemical composition, grain size, texture, defects are significant to determine its characteristics (Dermarkar *et al.*, 2006).

Reinforcements

There are several types of reinforcements (or fillers) available, such as ceramic (borides, carbides, nitrides, oxides) (Shuvho *et al.*, 2020), metal (Madhusudan *et al.*, 2016), metallic glass (Wang *et al.*, 2014b), intermetallic (Chaubey *et al.*, 2012), carbon-based (Xavior and Kumar, 2017), refractory metals (Yuan *et al.*, 2020), semiconductor, non-conventional such as egg-shell, ash or a combination of these materials depending upon the desired property such as strength, ductility, elastic modulus, density, thermal stability, compatibility with the matrix, electrical conductivity, etc. for end application. Metal matrix composites w.r.t the reinforcements can be classified into particulates (Aherwar *et al.*, 2020), interconnected type (Zhang *et al.*, 2020c), short fiber (Ding *et al.*, 2002)/whisker (Cao *et al.*, 1990), continuous fiber (Dutta, 2000), singular metal cored (Gupta and Sharon, 2010) and sheet reinforced (Gupta and Sharon, 2010) MMCs. With respect to the microstructure of the composite, factors such as the percentage of reinforcements, its type, shape, size, thermal expansion coefficient, orientation and distribution, etc. plays a significant role in

determining the properties (Dermarkar *et al.*, 2006). The properties can be estimated based on ideal conditions and not considering interaction between matrix and the reinforcement.

The reinforcement material should be uniformly distributed in the matrix to prevent localized plastic deformation and other local variation of properties (Arsenault *et al.*, 1991). Lloyd (1991) synthesized SiC reinforced AA6061 composites and observed localized strain and particle cracking in T6 tempered condition and it is attributed to SiC particle clusters that are subjected to triaxial stress and lead to premature failure of the material. Hence, the reinforcement distribution is very important.

Microstructural Evolution Using Different Reinforcement Materials

Fiber Reinforced MMCs

There are different types of fibers in MMCs like metal (Chang *et al.*, 2019), ceramic (Patil *et al.*, 2020), carbon, fiberglass (Samanta *et al.*, 2018), etc. The properties of the composite are isotropic for random orientation of discontinuous type fibers. For continuous type fibers, the properties are anisotropic for uni-direction alignment. Several other orientations such as multi-direction in-plane alignment exhibits isotropic properties. Apart from orientation, the behavior of MMCs also depends on the aspect ratio of the fibers (Shirvanimoghaddam *et al.*, 2017). Kim (2008) conducted elastic stress analysis to study the effect of fiber aspect ratio in short fiber-reinforced composites. He found significant effect of aspect ratio in composite strengthening mechanisms.

Continuous fiber composites can be classified into unidirectional (Chun and Daniel, 1997) or laminated (Chang *et al.*, 2019) composites, which in general exhibit enhanced strength but limited ductility (McWilliams and Yen, 2016). The fibers in general are strong compared to soft and ductile metallic matrix. The fibers can be randomly oriented also, as synthesized by Mizumoto *et al.* (2005) by dispersing SiC fibers in AZ91 alloy. Fiber arrangement plays a very important role in the mechanical response and Werwer *et al.* (1998) studied this phenomenon using finite elemental analysis. Three deformation mechanisms were stated for hexagonal, square and random arrangements, i.e., deformation with the orientation in a shear band (hexagonal and random), bowing-out mechanism (predominantly in square) and sharp bends (in non-regular arrangements). (Nardone and Prew, 1986) incorporated discontinuous SiC in Al and observed enhancement of yield strength. The difference in the thermal expansion coefficient of SiC and the matrix leads to an increased dislocation density.

Kurumlu *et al.* (2012) reinforced Al MMC with 15 vol% Al_2O_3 fibers synthesized using squeeze-casting method led to the formation of work hardened zones around fibers exhibiting increased dislocation densities during creep.

Samanta *et al.* (2018) used selective laser melting to fabricate glass fiber – reinforced metal matrix composites. The SEM images showed good fusion of glass fibers with Al matrix and these fiber bundles were uniformly covered by the melted powders of Al.

Particulate Composites

The reinforcement composed of particles of any configuration that are randomly distributed or dispersed with a defined orientation in a metallic matrix. Ibrahim *et al.* (1991) reviewed different processes used to synthesize particulate reinforced MMCs. They listed out several factors such as wetting, chemical interaction and reducing oxide formation to enhance interfacial bond strength in MMCs (Ibrahim *et al.*, 1991).

Ganesh *et al.* (Ganesh and Chawla, 2005) observed that the reinforced SiC particles get preferentially oriented along the extrusion axis of AA2080 composite that influences its tensile behavior. Increased volume fraction of SiC reinforced particles reduced the degree of orientation, and it was attributed to the reduced mean free path between SiC particles. This particle orientation anisotropy led to anisotropy in mechanical behavior and that was also validated using microstructure-based FEM modeling.

McNelly *et al.* (1977) devised fine-grained zinc based MMCs with increased volume fraction of W or Al_2O_3 particulate reinforcements and observed yield strengths of unusual values at low homologous temperatures and it is attributed to work hardening due to geometrically necessary dislocations generated by these stiff and incoherent particles.

Wu *et al.* (2019) conducted microstructure-based micromechanical modeling of fracture of SiC reinforced A359 MMC and identified important deformation and failure mechanisms by considering several factors related to particle geometry such as clustering distance and normalized shape factor. The particle clusters exhibited stress concentrations, especially close to the sharp edges and corners where particle fracture takes place.

Kelen *et al.* (2018) synthesized novel AZ91D alloy reinforced with TiNi alloy particles via hot-pressing. The microstructure consisted of α -solid solution, β - $\text{Mg}_{17}\text{Al}_{12}$ and TiNi particles, and although during processing, the constituents did not react with each other but they exhibited good bonding.

Huang *et al.* (2018) studied the microstructure and mechanical properties of tungsten carbide (WC) particle reinforced Al MMCs synthesized using friction stir processing (FSP). SEM images confirms the uniform bonding of WC with Al matrix. WC particles led to dynamic recrystallization and also hindered their growth.

Song *et al.* (Song and Huang, 2008) conducted experiments and simulations to study the effect of SiC particle size on the fracture toughness of Al MMCs. With increase in size and volume fraction of the reinforcement constituent, aging time and temperature, the fracture toughness decreases. This is because precipitation strengthening decreases the fracture toughness.

Wang *et al.* (2014a) synthesized a new particulate reinforced MMC comprising of soft Al matrix, soft alloy core such as Fe and hard intermetallic Al_5Fe_2 shell. Due to the enhanced ductility of the matrix and core, the crack tip gets blunt during crack propagation and overall the composite exhibits enhanced strength and plasticity.

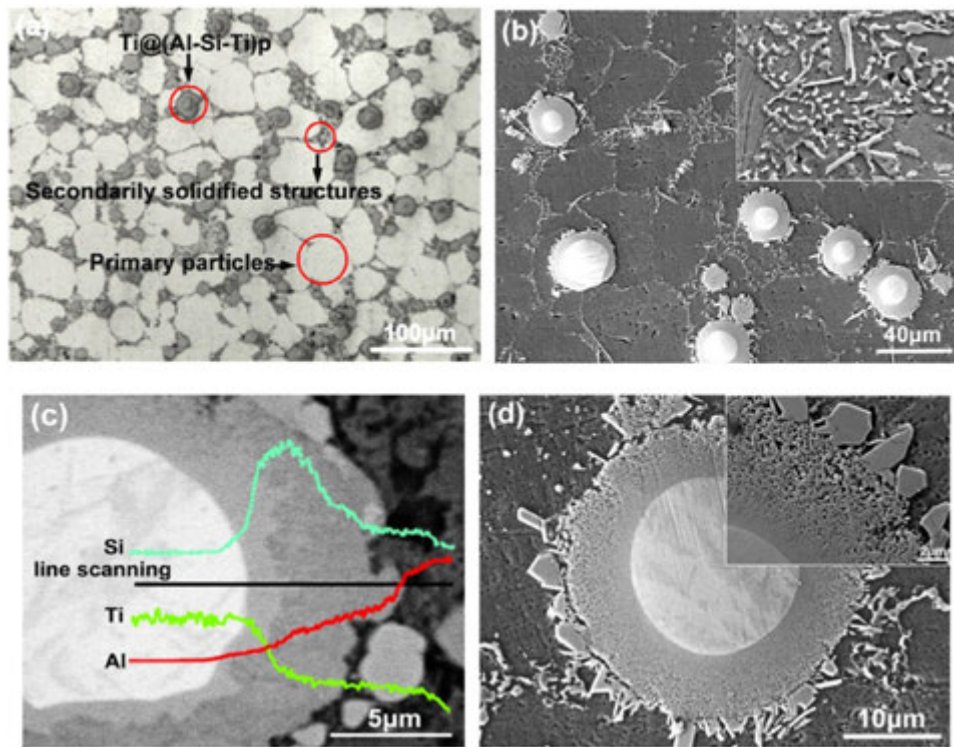


Fig. 1 Microstructures of as-fabricated composite: (a) optical microstructure, (b) scanning electron image, (c) back-scattered electron image and EDS analysis of one reinforcing particle and (d) SEM micrograph of one reinforcing particle. Insert in (b) is the morphology of corresponding eutectic Si phases and insert in (d) is the high magnification image of the particulate shell. From Zhang, J.Y., *et al.*, 2020b. Simultaneously strengthening and toughening a core-shell structured particulate reinforced aluminum alloy-based composite by solid solution treatment. *Journal of Alloys and Compounds*. 842, 155765. doi:10.1016/j.jallcom.2020.155765.

Zhang *et al.* (2020b) synthesized core-shell structured particle reinforced A356 alloy based Al MMC via powder thixoforming. The microstructure consists of Al-Si-Ti spheroidal phases with core-shell morphology, primary particles of α -Al, Mg_2Si , eutectic Si phases (needle like shaped as seen in the inset of Fig. 1(b)) and secondarily solidified structures (SSSs) as seen in Fig. 1. The core is rich in Ti and the shell consists of dual layered structure rich in Si and Al respectively as seen in EDS analysis in Fig. 1(c). Solution treatment reduced SSSs and dissolves eutectic Si. The primary α -Al particles and eutectic α -Al phases get interconnected. The Si rich ternary τ_1 ($\text{Al}_5\text{Si}_7\text{Ti}_{12}$) – phase particles transforms into Al-rich (Al, Si) $_3$ Ti-phase particles during solution treatment.

Nanocomposites

Lee *et al.* (2008) studied the microstructure and mechanical properties of in-situ nanocomposites made of Al-Fe system synthesized using press and sinter followed by friction stir processing (FSP). No Al-Fe reaction took place during sintering but during FSP, due to the short reaction time and severe plastic deformation (SPD) led to the formation of reinforcing particles $\text{Al}_{13}\text{Fe}_4$ in-situ. These particles were of micron sized ($\sim 1 \mu\text{m}$) and that led to the ultrafine grain structure of Al matrix.

Yao *et al.* (2015) synthesized SiC reinforced AA6063 composites using powder metallurgy route followed by hot-extrusion. Dynamic recrystallization of the matrix grains is attributed to the increased grain boundary energy present in the milled powders that provides the dynamic force, followed by the plastic deformation strain generated during hot-extrusion.

Li *et al.* (2020) studied the microstructural evolution of B_4C reinforced Ti MMCs using selective laser melting process (SLM). During this process, B_4C reacted with Ti matrix to form TiB whiskers or TiC particles and the former dominated due to poor solid solubility of B in Ti. 0.5 wt% B_4C addition led to a quasi-continuous structure whereas 1 wt% B_4C led to the formation of a continuous network structure.

Carbon nanotube reinforced MMCs

CNTs have increased values of surface area and if it is not uniformly dispersed, it will lead to clusters and hence inhomogeneous property distribution (Agarwal *et al.*, 2016). Bakshi *et al.* (Agarwal *et al.*, 2016) reviewed CNT reinforced MMCs and discussed the CNT dispersion and interfaces involved in different processing techniques such as ball milling, nanoscale dispersion, molecular-level mixing, spray drying, etc. Interface plays a very important role in engineering these composites as the load transfer to the reinforcement (fibers) from the matrix takes place across the interface (Piggott, 1989).

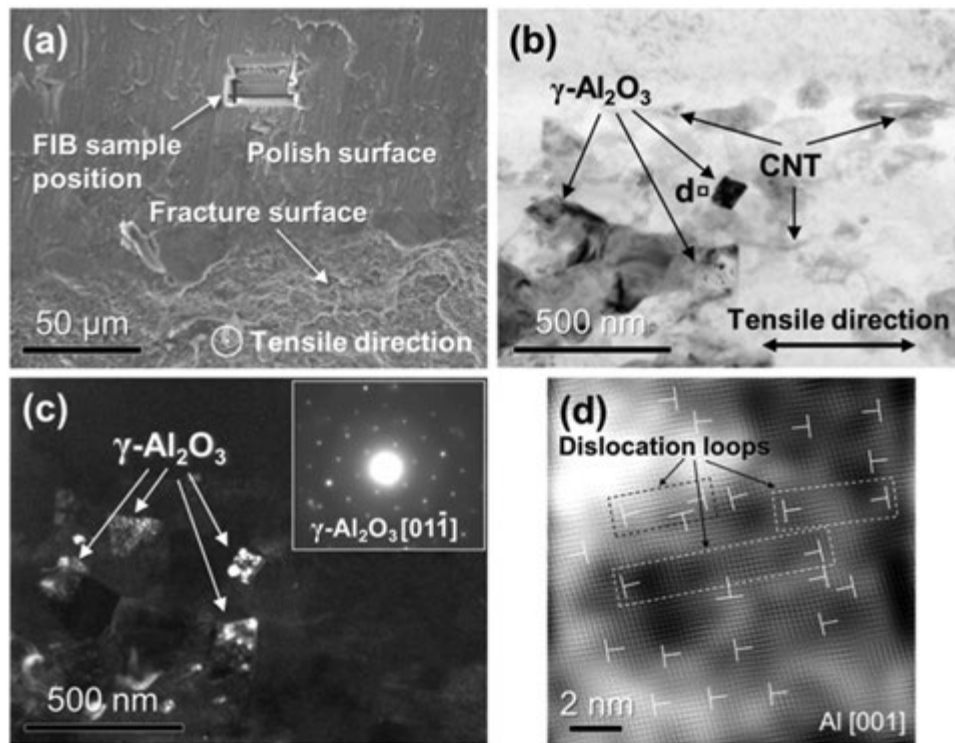


Fig. 2 TEM observations after tensile testing. (a) shows the position of a FIB sample on a tensile fracture surface. (b) Bright field and (c) corresponding dark field TEM images. (d) is an Inverse Fast Fourier Transform (IFFT) image showing a high density of dislocations generated in the Al matrix next to γ - Al_2O_3 nanoparticles. From Chen, B., *et al.*, 2020a Microstructure, tensile properties and deformation behaviors of aluminum metal matrix composites co-reinforced by ex-situ carbon nanotubes and in-situ alumina nanoparticles. Materials Science and Engineering A 139930. doi:10.1016/j.msea.2020.139930.

Chen *et al.* studied hybrid reinforcement of CNTs added ex-situ and in-situ ultrafine γ - Al_2O_3 nanoparticles formed using ball milling and spark plasma sintering (SPS) in Al MMCs (Chen *et al.*, 2020a). In-situ generated nanoparticles led to Orowan strengthening due to the presence of dislocation loops as seen in Fig. 2. During tensile deformation, formation of nanovoids appear around γ - Al_2O_3 nanoparticles that grow to form microvoids. CNT-induced bridging effect prevents further expansion of these microvoids that enhances the tensile ductility of the sample.

Laminate Composites

These are anisotropic as compared to particulate composites, which are isotropic in general. Several researchers synthesized laminate composites using different processes such as ARB (Wu *et al.*, 2010; Liu *et al.*, 2011; Chang *et al.* 2012; Habila *et al.*, 2019), hot-pressing (Zhu *et al.*, 2011), hot rolling (Zhang *et al.*, 2011a,b; Luo *et al.*, 2013). Different laminate composites such as coatings by laser cladding (Yan *et al.*, 2020), Al/Cu/Al joints using explosive welding (Hoseini Athar and Tolaminejad, 2015) have been synthesized for a variety of applications.

Liu *et al.* (2009) synthesized Mg-Al-Zn/Al laminated composites using equal channel angular extrusion (ECAE). The interface consisted of reaction phases such as Mg_2Al_3 and $\text{Mg}_{17}\text{Al}_{12}$ and with increased annealing temperatures the bonding layers got thickened.

Hu *et al.* (2020) first synthesized High Entropy Alloy (HEA)-intermetallic laminate composites formed between CoCrFeNi HEA and Al sheets prepared using solid diffusion welding. The SEM image as shown in Fig. 3 consists of three well-connected intermediate layers (L1, L2 and L3) formed between these sheets. L1 composed of fine equiaxed grains of Al_3Fe_2 -type, L2 composed of irregular and lath-shaped of $\text{Al}_{13}\text{Fe}_4$ -type. L3 exhibited dual-phase structure of $\text{Al}_{13}\text{Cr}_2$ -type and $\text{Al}_{13}\text{Fe}_4$. These intermetallic layers exhibited an increased hardness values as compared to HEA and Al sheets.

Porous Materials

To create light materials for applications that require increased compressibility or low Young's modulus, porosity is desired. Several studies have been carried out in this area, especially on lightweight materials. Batista *et al.* (2019) synthesized MWCNT reinforced porous Al MMCs using cold pressing followed by sintering for wear resistant hard coatings. Dele-Afolabi *et al.* (2018) developed alumina-Ni composites of porosity close to 57% using rice husk (RH) and sugarcane bagasse (SCB) as pore forming agents. Formation of a $\text{Ni}_3\text{Al}_2\text{SiO}_8$ (spinelloid) phase in RH type and NiAl_2O_4 spinel in SCB type led to fine and dislocated grain

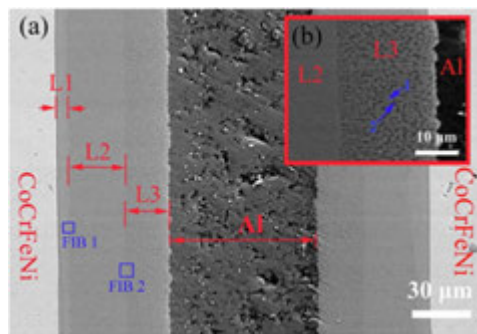


Fig. 3 SEM photograph of the CoCrFeNi/Al HILC. From Hu, Y., *et al.*, 2020. Microstructure characteristics of a high-entropy-alloy intermetallic laminate composite. *Materials Letters* 273, 127937. doi:10.1016/j.matlet.2020.127937.

structures respectively. Porous structures can aid in biocompatibility, as studied by Chasali *et al.* (2019) for Al_2O_3 whiskers and Si_3N_4 particle reinforced Mg MMCs prepared via microwave sintering. Ethylene glycol was used as space holder agent that led to the formation of porous structure.

Microstructural Evolution During Processing

Fabrication techniques can be classified into solid, liquid, gas state and in-situ processes (Bauri *et al.*, 2018). Some of the methods in solid-state processing include powder metallurgy methods (wet and dry method), diffusion bonding, mechanical alloying, spark plasma sintering etc. Casting, liquid infiltration, preform impregnation, spray deposition, pressureless infiltration, ultrasonic infiltration belong to the category of liquid-state processing. Deposition techniques such as chemical vapor deposition, physical vapor deposition are some of the gaseous methods. The microstructural aspects of some of these techniques is discussed.

Casting

Near net shaped fabrication, uniform distribution of reinforcements and control in solidification conditions are some of the advantages of casting route for material synthesis. Particle distribution during casting is influenced by several factors like agglomeration, sedimentation, melt rheology, matrix-particle interactions, etc. (Hashim *et al.*, 2002). Particle-matrix interactions can be long-range and short-range in the form of solute field interactions (Sekhar and Trivedi, 1991) and viscous drag forces respectively (Asthana and Tewari, 1993). It also influences the microstructure by altering the solute concentration gradient near the tip of dendrite and hence affecting the advancing interface (Dutta and Surappa, 1998). Sekhar *et al.* (Sekhar and Trivedi, 1991) observed dendritic tip splitting or dendritic to cellular transition with the presence of reinforcements. Surappa (1997) studied the solidification processing used for synthesizing discontinuously reinforced metal matrix composites (DRMMC). Among different possible microstructures, he classified the solidification front into plane, cellular and dendritic, which is illustrated in Fig. 4. Under different solidification conditions like engulfment (uniform distribution) and entrapment (micro segregation), he discussed the concept of particle distribution map by adapting different process parameters.

A growing crystal during solidification could either reject or engulf the particle (Asthana and Tewari, 1993) and this is based on fluid dynamics, thermodynamics, surface chemistry and other interaction phenomena. In Fig. 4, the dendritic solidification front looks complicated with different possibilities of microstructures w.r.t the interaction with either primary or secondary dendritic arm.

Liquid Infiltration

To incorporate large volume fraction of reinforcement and synthesize materials with complex shapes, a liquid phase (molten metal matrix) fills the gap between the reinforcement material such as ceramic particles, fibers, etc., via capillary force or an external pressure (Sree Manu *et al.*, 2016). There are several categories of infiltration process such as pressure die, gas pressure, ultrasonic, centrifugal, lorentz force and squeeze casting.

Shin *et al.* (2019) studied the evolution of microstructure of monomodal and bimodal sized SiC reinforced T6 treated Al7075 composites synthesized using liquid-pressing process. Hard spherical Mg_2Si precipitates were dispersed homogeneously in the matrix that reduced to smaller sizes during the precipitation hardening.

Lee *et al.* (2020) synthesized TiC- (JIS SKD11) steel composite using this process and studied the microstructure and mechanical properties. The SEM micrographs of TiC powder, preform and the composites are presented in Fig. 5. Irregular shaped TiC (Fig. 5(a)) were then pressed to create a preform and sintered (Fig. 5(b)). These preforms are placed along with steel ingots in the crucible and heated by vacuum induction melting. Later they are pressurized using argon gas, followed by pouring into the mold. A homogeneous distribution of the reinforcement can be observed in Fig. 5(c). Due to the dissolution and re-precipitation

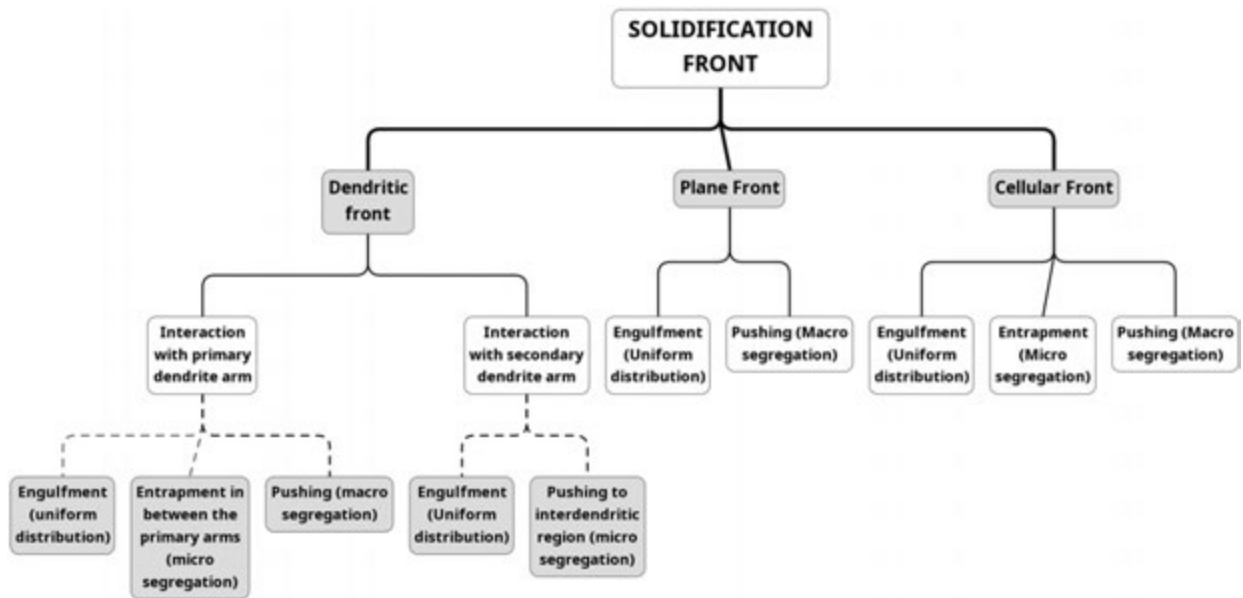


Fig. 4 Schematic showing various possible microstructures in a composite casting. Adapted from Surappa, M.K., 1997. Microstructure evolution during solidification of DRMMCs (discontinuously reinforced metal matrix composites): State of art. *Journal of Materials Processing Technology*. 63, 325–333. doi:10.1016/S0924-0136(96)02643-X.

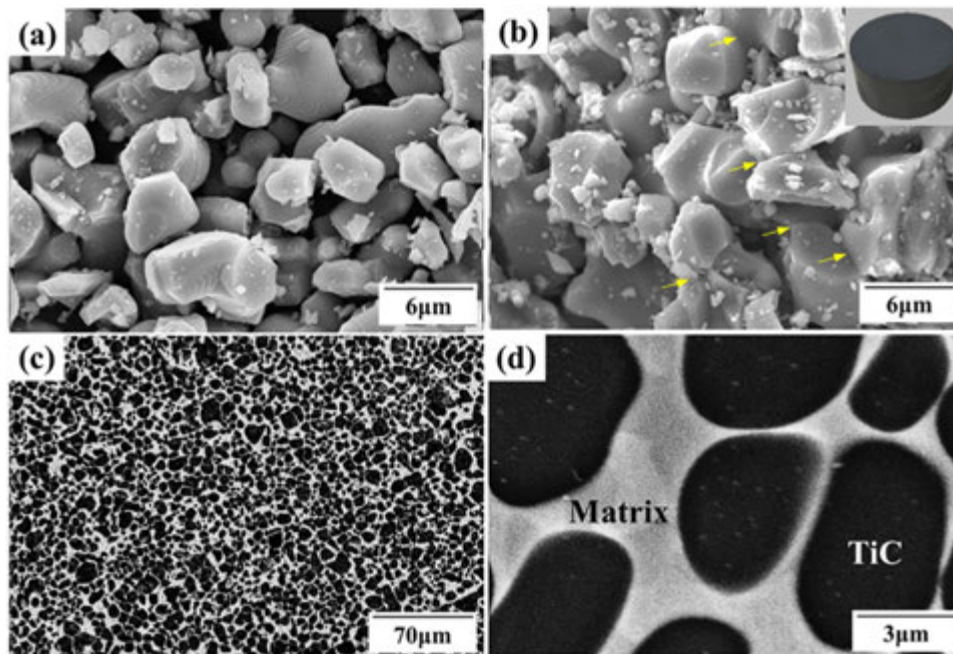


Fig. 5 Microstructure of (a) raw TiC powders, (b) sintered TiC preform, and (c, d) TiC-SKD11 composites fabricated by the LPI process. From Lee, Y.H., *et al.*, 2020. Microstructure and mechanical properties of lightweight TiC-steel composite prepared by liquid pressing infiltration process. *Materials Characterization*. 162, 110202. doi:10.1016/j.matchar.2020.110202.

of the reinforcement, a core-rim microstructure can be seen in **Fig. 6**. Nanoindentation tests carried out at the core-rim interfaces exhibited similar trends compared to the tests on the hard TiC cores.

Preform Impregnation Process

This process involves replication of structure of a material with the metal (mortar), adsorption of brick material into the mortar followed by hot-compaction. Xiong *et al.* (2015) synthesized bioinspired graphene and copper artificial nacre metal matrix

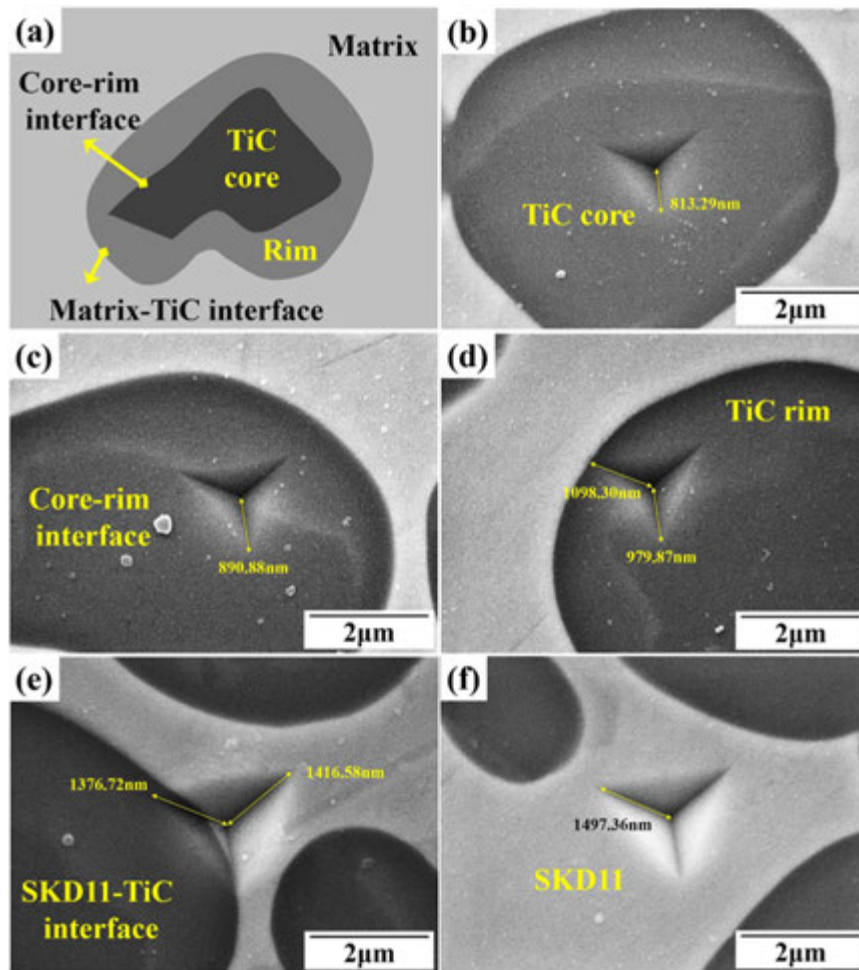


Fig. 6 (a) Schematics and detailed microstructure of impression after nano-indentation on (b) TiC core; (c) TiC core-rim interface; (d) TiC rim; (e) TiC/SKD11matrix interface; and (f) matrix alloy. From Lee, Y.H., *et al.*, 2020. Microstructure and mechanical properties of lightweight TiC-steel composite prepared by liquid pressing infiltration process. *Materials Characterization*. 162, 110202. doi:10.1016/j.matchar.2020.110202.

composite. Copper was first replicated to that of an ordered porous structure made of fir wood, followed by reduced graphene oxide (RGrO) absorption into this porous preform and then compaction using hot-pressing method. As seen in Fig. 7, the composite exhibited brick (RGrO) and mortar (copper) type microstructure. RGrO was dispersed homogeneously and aligned in Cu matrix due to smaller wall thickness of ordered pores.

Spray Deposition

This process involves depositing atomized stream of particulate containing molten metal onto the substrate (White and Willis, 1989). The process parameters that can influence the microstructural evolution are atomization temperature, melt stream diameter, spray height, substrate's rotational velocity, atomization gas pressure and powder transportation pressure (Chen *et al.*, 2009). This method of synthesis ensures less relative contact time between the molten metal and the reinforcement and therefore they exhibit enhanced metal-ceramic interface integrity (White and Willis, 1989).

Chen *et al.* (2009) studied the microstructural evolution of SiCp/Al-8.5Fe-1.3V-1.7Si developed using spray co-deposition technology. The microstructures of both as-deposited and extruded materials exhibited lamellar morphology, which was attributed to the substrate's rotation during deposition. It was also denoted as tree ring structure (TRS) and it consisted of bands of low and high particle concentrations.

Selective Laser Melting (SLM)

This technique uses a powered laser to melt the powders and fuse them together (Ivanov *et al.*, 2017; Zhao *et al.*, 2018). Several parameters such as laser power, scan speed etc. could be tailored to achieve different microstructures (Khorasani *et al.*, 2019). Rong *et al.* (2016) synthesized WC reinforced Inconel 718 composites using SLM with a novel graded interface with a diffusion layer

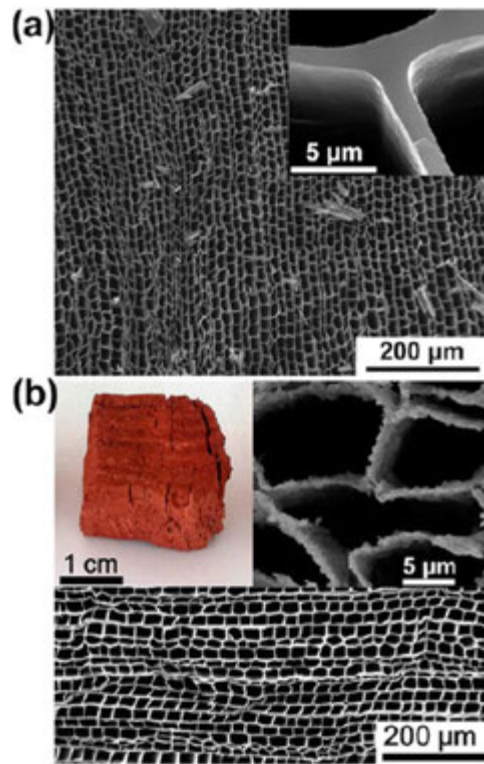


Fig. 7 (a) Layered porous structure of fir wood (the wood was carbonized for SEM observation). (b) Monolithic fir-templated porous Cu preform with a typical size of $2 \times 1.5 \times 1.5 \text{ cm}^3$. High and low magnification SEM images indicate a good replication of the microstructure of fir wood. From Xiong, D.B., *et al.*, 2015. Graphene-and-copper artificial nacre fabricated by a preform impregnation process: Bioinspired strategy for strengthening-toughening of metal matrix composite. ACS Nano 9, 6934–6943. doi:10.1021/acs.nano.5b01067.

formed due to in-situ reaction between the constituents. This changed the wear mechanism to adhesive from severe abrasive and enhanced the wear performance of the composite.

Chen *et al.* (2020c) synthesized in-situ TiC/Inconel 625 nanocomposites using selective laser melting process and studied the effect of laser fluence on the microstructure. “Fish-scale” morphology in IN625 was observed and the columnar dendrites get refined with increased laser fluence values. Increased dislocation density was observed due to the difference in CTE between the matrix and the reinforcement.

In-Situ Processes

To eliminate the brittle layer at the matrix-reinforcement interface and create fine particulate reinforcements with uniform distribution, composites synthesized using in-situ processes exhibit enhanced mechanical properties (Yang *et al.*, 2003; Wang *et al.*, 2004; Tian *et al.* 2014).

Ma *et al.* synthesized TiB_2 reinforced Al-Zn-Mg-Cu composite using an in-situ mixed salt method consisting of dipotassium titanium hexafluoride and potassium fluoroborate (Ma *et al.*, 2020). The TEM image of the composite shows uniform distribution of TiB_2 nanoparticles in the matrix as seen in Fig. 8(a). The interface precipitation was governed by the faceted TiB_2 nanoparticles (Fig. 8(b)) that led to effective interface strengthening by minimizing the mismatch of the interface and maximizing the coherency.

Powder-Metallurgy Processing

Problems with wetting and interfacial bonding in conventional methods of synthesis could be overcome in powder-metallurgy processing (Manohar *et al.*, 2018). Zhang *et al.* (2020a) used SiC-graphite and SiC-graphene as reinforcements into A355 Al-Si alloy matrix using powder metallurgy route comprising ball milling, compaction and hot-pressing. Microstructural evolution of bulk composites comprised of carbonaceous defects formed during ball milling, well dispersed SiC-graphene nanosheets and the formation of Al_4C_3 needles during hot pressing. Fig. 9 shows TEM micrograph of Al-Gt (A355 + SiC + graphite) and Al-Gn (A355 + SiC + graphene nanosheets). A nanostructured composite with an uniform distribution of reinforcement is obtained.

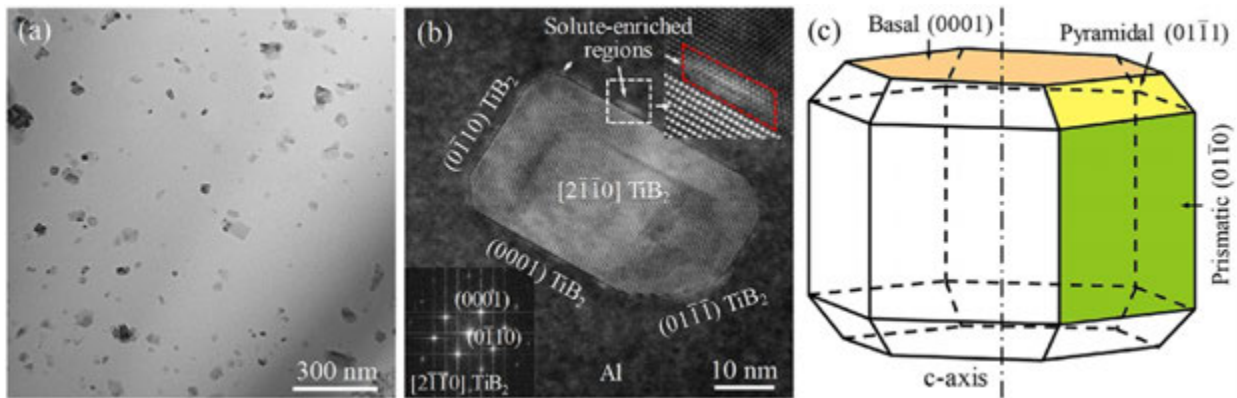


Fig. 8 (a) Bright-field TEM image showing homogenous distribution of TiB₂ nanoparticles in the Al-Zn-Mg-Cu matrix grain, (b) STEM-HAADF image showing a typical TiB₂/Al interface at the as-quenched state and (c) schematic drawing illustrating the faceted shape of the TiB₂ nanoparticle. Insets in (b) at the left bottom and top right sides highlight corresponding FFT pattern of the TiB₂ nanoparticle and solute-enriched regions, respectively. From Ma, Y., *et al.*, 2020. Atomic-scale investigation of the interface precipitation in a TiB₂ nanoparticles reinforced Al-Zn-Mg-Cu matrix composite. *Acta Materialia*. 185, 287–299. doi:10.1016/j.actamat.2019.11.068.

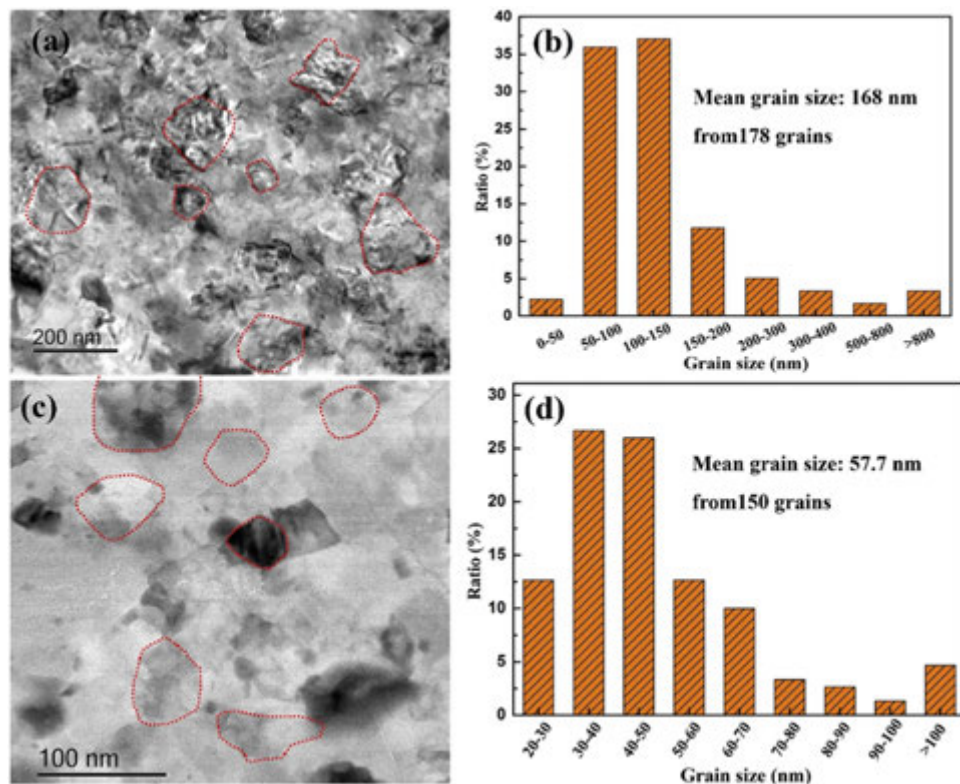


Fig. 9 TEM images of (a) Al-Gt and (c) Al-Gn. The Al grain size distribution of (b) Al-Gt and (d) Al-Gn. From Zhang, J., 2020a. Microstructural evolution of hybrid aluminum matrix composites reinforced with SiC nanoparticles and graphene/graphite prepared by powder metallurgy. *Progress in Natural Science: Materials International*, 1–8. doi:10.1016/j.pnsc.2020.01.024.

Secondary Deformation Processing

Bulk-forming and sheet-forming constitute secondary deformation processes, where the tool and surfaces of the deforming material are always in contact. MMCs can be synthesized using several processes, like extrusion, forging and rolling etc.

Extrusion

Extrusion can lead to discontinuous fibers to align in the axial (extruded) direction preferentially and this process can break down the reinforcements, reduce porosity and enhance bonding. Uan *et al.* (2001) synthesized in-situ Al-Al₃Ni composite using

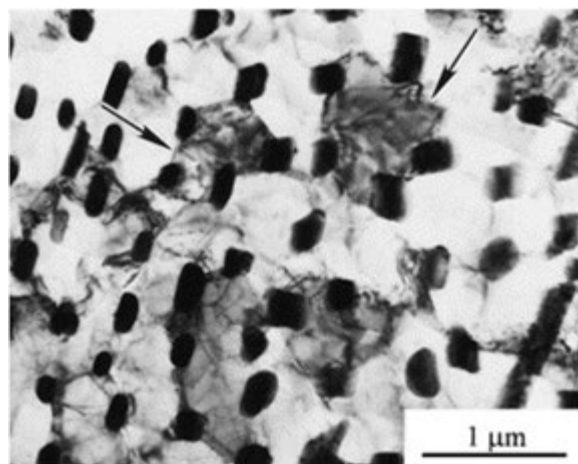


Fig. 10 EU200, transverse section of position 1 which shows numerous tangled dislocations and many of them pinned by adjacent Al_3Ni particles. The subgrains are marked by two arrows. From Uan, J.Y., Chen, L.H., Lui, T.S., 2001. On the extrusion microstructural evolution of Al- Al_3Ni in situ composite. *Acta Materialia*. 49, 313–320. doi:10.1016/S1359-6454(00)00309-8.

directional solidification and studied the microstructural evolution post extrusion at 200°C and 400°C. Microstructures at 200°C composed of tangled dislocations pinned by Al_3Ni fibers in the presence of small subgrains as seen in Fig. 10 whereas at higher temperatures they evolve upto 3–4 μm that have low density of dislocations. The polygonization process is depicted in Fig. 11.

Forging

Forging is a deformation process involved with localized compressive forces, which can be carried out with or without the application of heat (Ozerov *et al.*, 2019).

Deng *et al.* (2010) studied hot forged SiCp/AZ91 composites synthesized using stir casting route. Fig. 12 shows the optical microstructures of as-cast and as-forged composites at different temperatures. Hot forging enhanced the particle distribution and it led to basal texture formation that weakened with increased forging temperatures. Deformed structures decrease and finer equiaxed grain structure increase with temperature. These uniformly distributed SiC particles activated dynamic recrystallization and this phenomenon improved with temperature.

High pressure torsion (HPT)

The materials in this technique are subjected to compressive forces similar to that of forging, but they are also subjected to torsional straining (Zhilyaev and Langdon, 2008). Aristizabal *et al.* (2020) subjected CNT reinforced Ni matrix composites under high pressure torsion (HPT) and studied their microstructural evolution. Formation of nickel carbide was observed in these composites with enhanced thermal stability and CNTs restricted the grain growth at higher temperatures.

Kawasaki *et al.* (2016) stacked disks of Al-1050 and ZK60A and processed using HPT. This process introduces a lot of vacancy-type defects and this leads to lower activation energy for diffusion bonding of Al and Mg phases.

Equal channel angular pressing (ECAP)

This technique involves severe plastic deformation but without changing the geometry of the specimen (Semenova *et al.*, 2018). Abbas *et al.* (Abbas and Huang, 2020) studied the microstructure of AZ91 MMCs reinforced with WS_2 prepared using stir casting method followed by ECAP. The microstructures consisted of α -Mg, Al_5Mn_3 , WS_2 , β - $\text{Mg}_{17}\text{Al}_{12}$ and Mg_2Al_3 . The precipitation was discontinuous and it is attributed to the cellular breakdown of secondary precipitates. Increased ECAP passes induced cracks in the precipitates.

Diffusion Bonding

Diffusion bonding comprises of plastic deformation of asperities, followed by change in void morphology close to the bonding interface and finally their contraction and the removal (Derby and Wallach, 1984). Vacuum hot pressing (VHP), step pressing, hot-die molding, superplastic forming, hot isostatic pressing are few examples of the synthesis methodologies (Everett and Arsenault, 1991).

He *et al.* (2003) used diffusion bonding method to produce a TiAl/steel composite with barrier layers using foils of V, Cu and Ti. The synthesis was carried out using a vacuum induction heating machine. At the interface of TiAl/Ti, a dual phase $\text{Ti}_3\text{Al} + \text{TiAl}$ and solid solution of Ti was formed that contributed to increased strength.

Guo *et al.* (Guo and Derby, 1993) used diffusion bonding consolidation method to fabricate Ti-6Al-4V/SiC fiber composite. At 870°C, it exhibited complete matrix-matrix bonding with fine and equiaxed ($\alpha + \beta$) structure. Below 770°C, due to poor inter-diffusion it does not provide good composite bonding. Above 1070°C, SiC crystals and grains grow that reduce the properties of the composite.

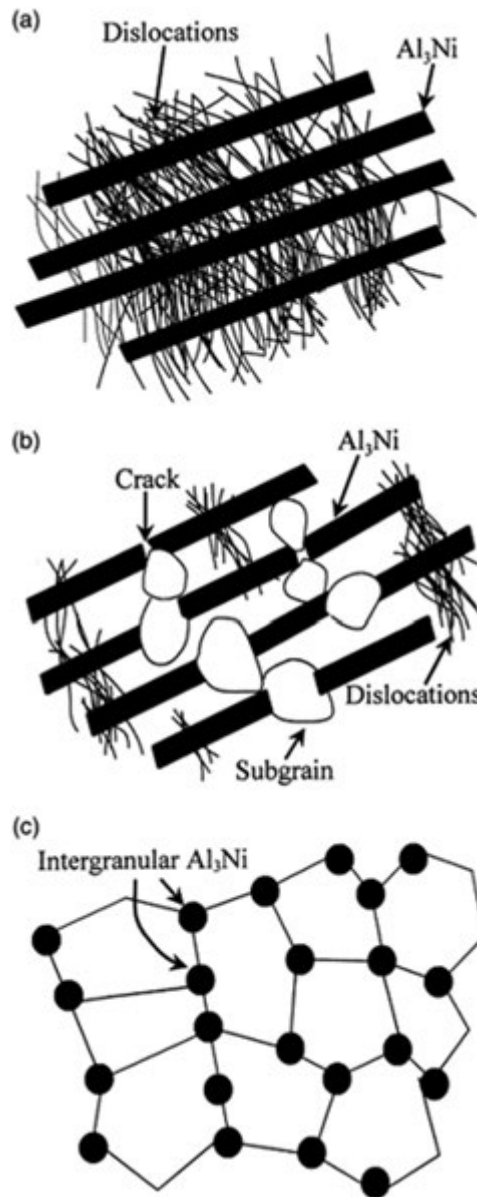


Fig. 11 Schematic diagrams showing the microstructural evolution during 200°C extrusion [(a) and (b): longitudinal sections; (c): transverse section]. From Uan, J.Y., Chen, L.H., Lui, T.S., 2001. On the extrusion microstructural evolution of Al-Al₃Ni in situ composite. *Acta Materialia*. 49, 313–320. doi:10.1016/S1359-6454(00)00309-8.

Accumulative Roll Bonding (ARB)

A severe plastic deformation technique involving rolling, ARB involves processes such as degreasing and wire-brushing, stacking, roll-bonding, cutting and these steps are repeated (accumulated) (Tsuji, 2011). Danielle *et al.* (Magalhães *et al.*, 2020) synthesized AA1050/AA7050 multilayered composites using Asymmetric Accumulative Roll-Bonding (AARB) technique. Initial rolling of AA1050 in room temperature was followed by annealing whereas the overaged AA7050 was rolled at higher temperatures (400°C). The former alloy exhibited equiaxed grain structure whereas the latter had elongated grain structure. Fig. 13 shows different microstructures generated after AARB treatment with different preheating conditions and different number of cycles. The interface zone shows no debonding and due to asymmetric conditions, layers exhibit wavy-patterns.

Chen *et al.* (2015) investigated the deformation inhomogeneities of AZ31 – AA1100 laminated composites that arise due to the different deformation behavior of metals. Initial ARB cycles saw local necking in Mg layers, which saw more fractures. Hence, layers of AZ31 gets bent and discontinuous whereas Al layers fill the neighboring region. Final microstructure consists of a continuous soft Al matrix with hard Mg laminated fragments.

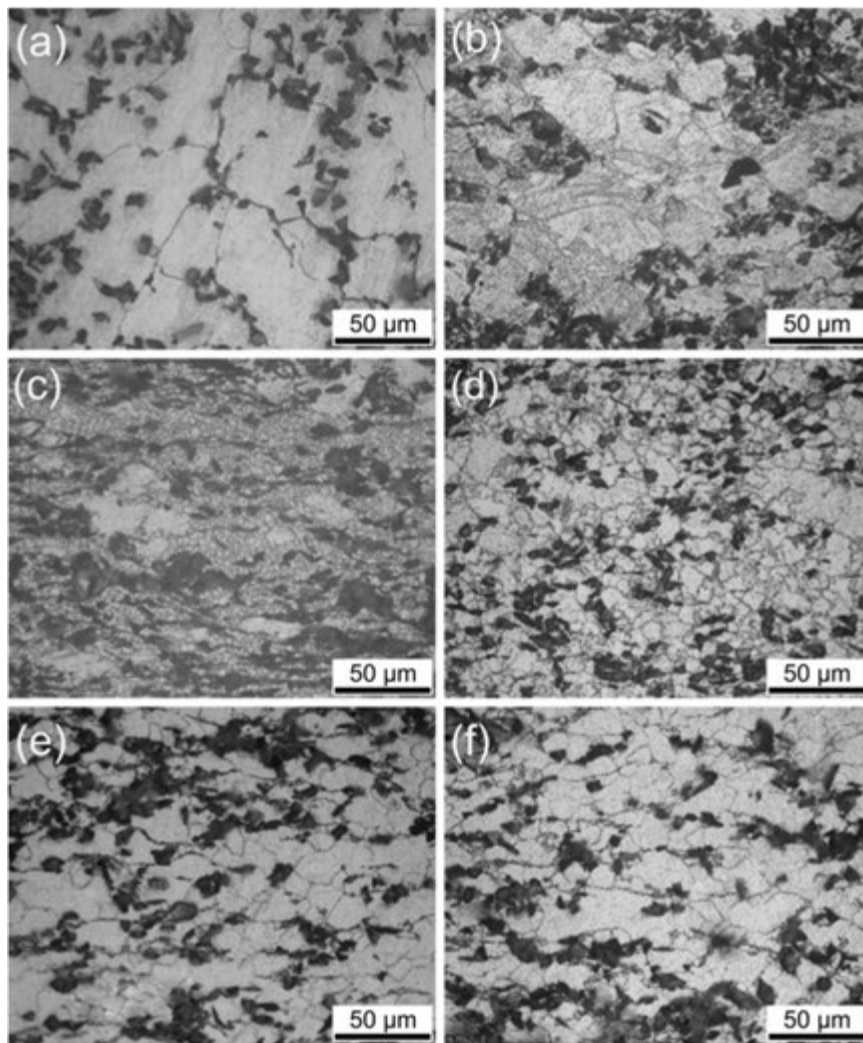


Fig. 12 Optical micrograph of SiCp/AZ91 composite of (a) as-cast and as-forged at the temperatures of (b) 320°C, (c) 370°C, (d) 420°C, (e) 470°C and (f) 520°C. From Deng, K.K., *et al.*, 2010. Microstructure evolution and mechanical properties of a particulate reinforced magnesium matrix composites forged at elevated temperatures. *Materials Science and Engineering A* 527, 1630–1635. doi:10.1016/j.msea.2009.10.053.

Explosive Shock Consolidation

By using shock waves, this process results in interparticle bonding due to powders subjected to severe deformation (Meyers and Wang, 1988). Raghukandan *et al.* (2004) prepared Al- 30 vol%SiC_p composites using underwater shock consolidation method by adapting detonation velocity of 6.9 km/s. Microstructures did not consist of reaction products like brittle Al₄C₃ that is sensitive to corrosion and mostly detrimental. The high shock energy led to high consolidation pressure of about 7 GPa which densified the composite.

Vorozhtsov *et al.* (2017) used nanodiamonds and aluminum nanoparticles and synthesized composites with high density and enhanced mechanical properties. A schematic of explosive consolidation process is shown in Fig. 14 where deformation flows remove the oxide layer and the nanodiamond particles exert compressive force on the aluminum particles, which leads to the formation of metastable aluminum phase.

Plating and Deposition Techniques

Electrodeposition

A bottom-up approach involved in depositing ions reduced at the cathode, electrodeposition technique can be used to prepare MMCs with high purity. Rekha *et al.* (Rekha and Srivastava, 2019) studied microstructural evolution of ZnNi-GO composite coatings synthesized using electrodeposition technique. Several intermetallic phases like γ -NiZn₃, δ -Ni₃Zn₂₂, and γ -Ni₅Zn₂₁ were identified in ZnNi-GO coatings along with pure Zn phase nucleated and grew over GO.

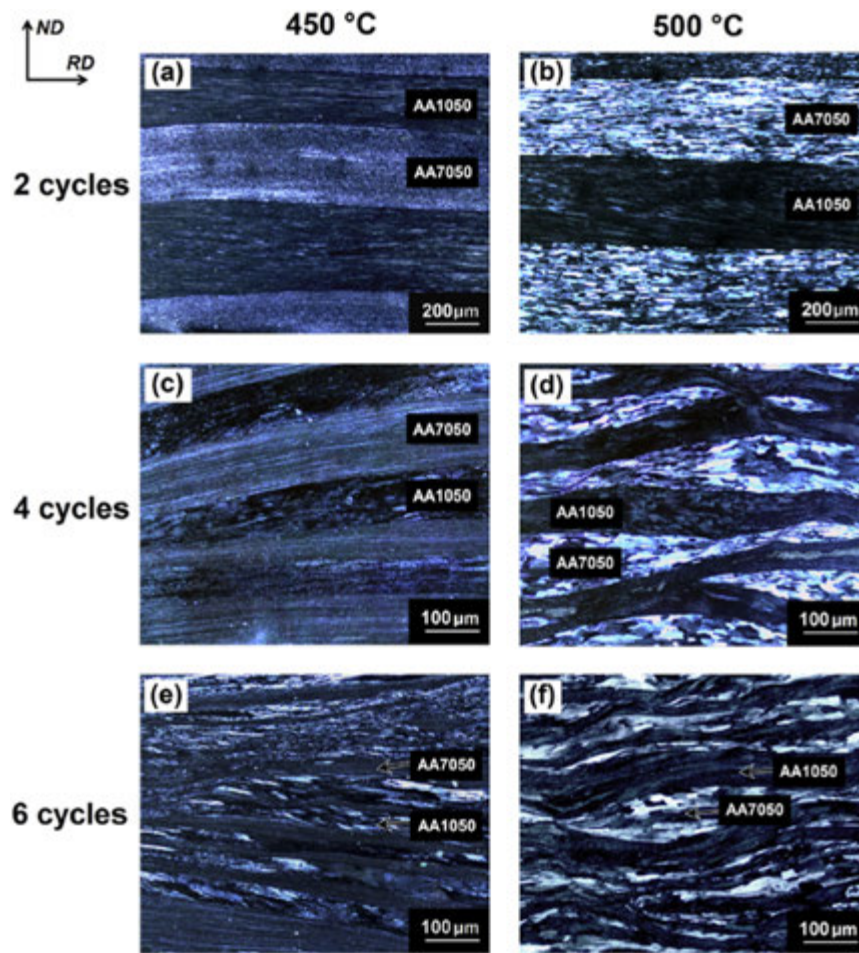


Fig. 13 Microstructural evolution of the multilayered composite sheets of AA1050/AA7050 Al alloy processed after a different number of cycles at: (a, c, e) 450 °C; and (b, d, f) 500 °C. ND = normal direction and RD = rolling direction. From Magalhães, D.C.C., Sordi, V.L., Kliauga, A.M., 2020. Microstructure evolution of multilayered composite sheets of AA1050/AA7050 Al alloys produced by asymmetric accumulative roll-bonding. *Materials Characterization* 162, 110226. doi:10.1016/j.matchar.2020.110226.

Wang *et al.* (2020) developed layered CNT/Cu composites with heterostructures using electrodeposition, followed by spark plasma sintering. Optimizing CNT content in the layered films was carried out by tailoring the deposition current density. The mechanical properties exhibited a balance between the strength and ductility due to this microstructure.

Wang *et al.* (2019) developed activated carbon (AC) reinforced Ni MMCs using facile electrodeposition technique for electrode applications. Ni films without AC exhibited elongated and flaky structure and with AC showed a cactus like 3D flower like morphology that enhanced the surface area, which is beneficial for hydrogen evolution reactions.

Chemical vapor deposition (CVD)

CVD method is a vacuum deposition technique that can homogeneously deposit materials using precursors that vaporize and react with each other to form composites. One of the first fabrications of carbon fiber reinforced Al MMCs were carried out by Baker *et al.* (1972) and Jackson *et al.* (1972). They used CVD from tri-isobutyl aluminum to develop Al coated C fibers.

He *et al.* (2009) synthesized CNT reinforced Al MMCs using CVD technique, as shown in the microstructure in Fig. 15. The morphology of in-situ synthesized CNT-Al powders is spherical as seen in the SEM image in Fig. 15(a). Apart from the uniform dispersion of CNTs due to this technique, the formation of Al_4C_3 as a thin layer at the interface provides good interfacial bonding.

Ultrasonic Treatment

The technique of ultrasonication has been used for refinement of the microstructure (Yang *et al.*, 2018), dispersion of reinforcement via transient cavitation and acoustic streaming (Yang *et al.*, 2004), removal of hydrogen (Liu *et al.*, 2017), etc.

Hu *et al.* (2018) used ultrasonic treatment prior to squeeze casting to synthesize nano-SiCp reinforced A356 composites. A356 consist of acicular long heterogeneously distributed eutectic Si and coarse dendrites of primary $\alpha(\text{Al})$. Addition of SiCp reduced the

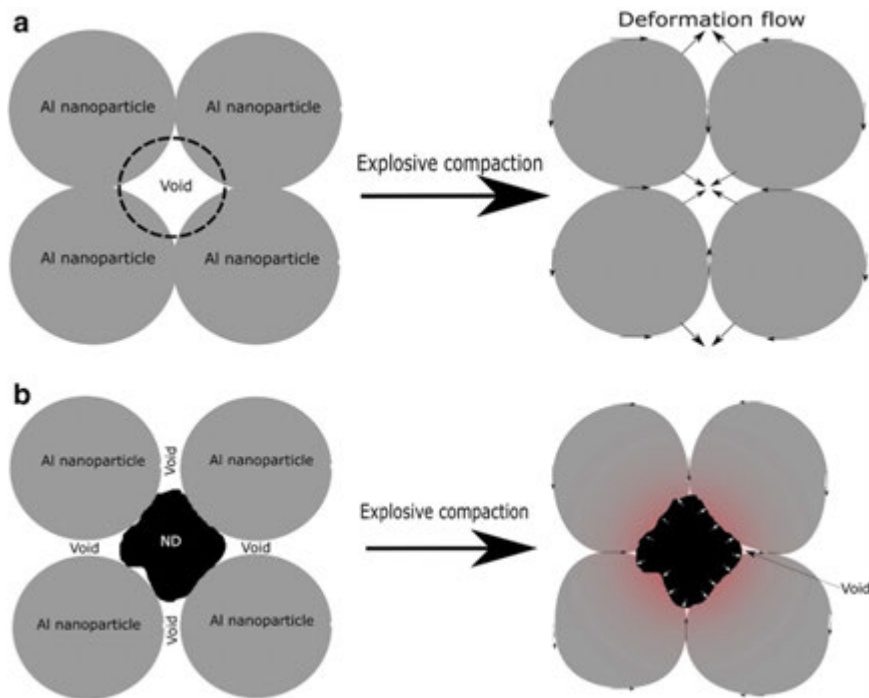


Fig. 14 Schematic of the consolidation process of nanopowders under explosive compaction. From Vorozhtsov, S., *et al.*, 2017. Structural and mechanical properties of aluminum-based composites processed by explosive compaction. *Powder Technology* 313, 251–259. doi:10.1016/j.powtec.2017.03.027.

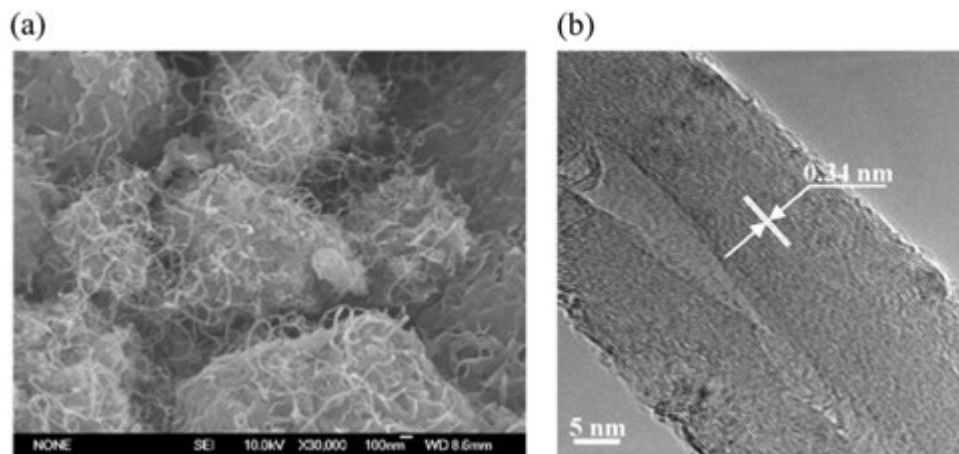


Fig. 15 (a) SEM image of a CNT–Al composite powder, (b) HRTEM image of a typical CNT, showing a well-graphitized multiwalled nanotube. From He, C.N., *et al.*, 2009. Mechanical properties and microstructures of carbon nanotube-reinforced Al matrix composite fabricated by in situ chemical vapor deposition. *Journal of Alloys and Compounds*. 487, 258–262. doi:10.1016/j.jallcom.2009.07.099.

dendrite length and refines eutectic Si. These dendrites change their morphology to rosette crystals and equiaxed grains. Uniform distribution of nano-SiCp takes place due to ultrasonic treatment, as shown in the schematic in Fig. 16(a). Nucleation of primary $\alpha(\text{Al})$ takes place when the melt is close to the liquidus temperature and dendritic growth is restricted by the nano-SiC particles.

Different Types Microstructures Involved

In this section, the microstructures of composites with Al, Mg and Ti matrix configurations are discussed. Al and Mg based composites are lightweight and are used in aerospace and automotive applications whereas Ti based composites are commonly used for high-temperature applications.

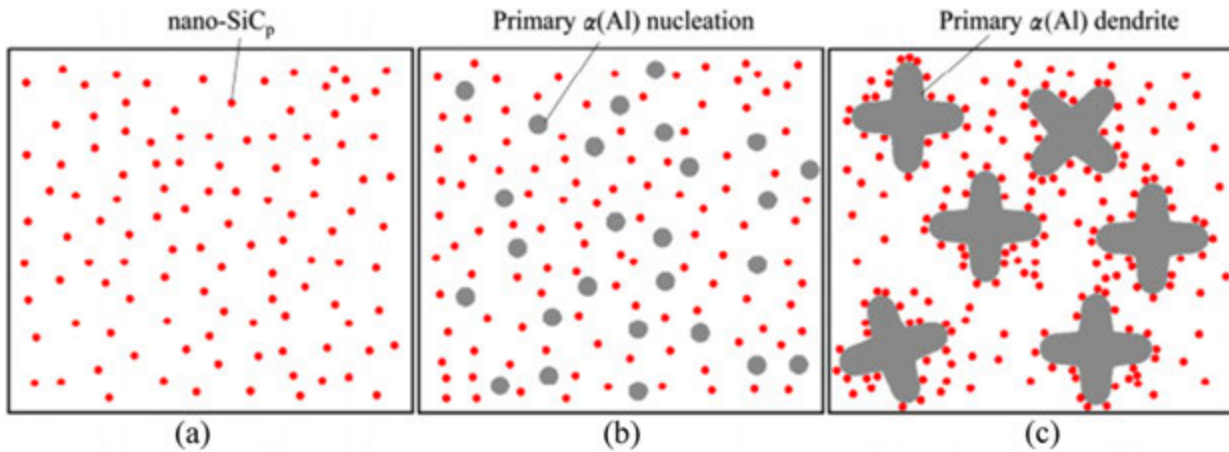


Fig. 16 Schematic diagram of microstructure evolution of nano-SiCp/A356 composite melt before eutectic reaction: (a) Uniformly distributed nano-SiCp in composites melt; (b) Nucleation of primary $\alpha(\text{Al})$; (c) Growth of $\alpha(\text{Al})$ grains. From Hu, K., *et al.*, 2018. Effects of nano-SiCp content on microstructure and mechanical properties of SiCp/A356 composites assisted with ultrasonic treatment. Transactions of Nonferrous Metals Society of China. 28, 2173–2180. doi:10.1016/S1003-6326(18)64862-9.

Aluminum Metal Matrix Composites

Aluminum is lightweight, has good thermal conductivity and has excellent corrosion resistance. Chidambaram *et al.* described the metallographic preparation of aluminum-alumina MMCs (Chidambaram and Bhole, 1997). Since these reinforcement materials are hard particles, conventional alloy polishing practices cannot be perceived. Among several methods, Buehler method that involved grinding on SiC paper followed by diamond polishing on cloth and etching with 5% HF (49%) in distilled water was optimum for revealing the microstructure.

Kundu *et al.* (2013) studied the microstructure of SiC reinforced Al MMCs prepared using manual stir casting. Microstructural analysis showed uneven distribution of SiC which was attributed to the difference in its density between molten metal.

Xiao *et al.* (2019) studied the microstructural evolution of a hypereutectic Al-20Si alloy containing x wt% TiB_2 particles. The microstructure consisted of eutectic structures with primary Si phase and TiB_2 particles not only acted as substrate for heterogeneous nucleation of primary Si, but also hindered element diffusion and restricted its growth.

Chelliah *et al.* (2017) used liquid stir-casting method and injected cross-linked polymer powder into Mg, AZ91 and AE44 alloys to synthesize in-situ SiCNO phases in Mg MMCs. The microstructural evolution of PP900-AE composite specimen is shown in Fig. 17. Coarse sized Mg_2Si crystals are dispersed along with acicular Al_xRE_y as shown in Fig. 17(a).

Magnesium Metal Matrix Composites

Magnesium based alloys and composites are widely used in automobile, biomedical, electromagnetic shielding and other specialty applications. Horvitz *et al.* (Horvitz and Gotman, 2002) used self-propagating high-temperature synthesis (SHS) to develop in-situ MgAl_2O_4 – TiAl composites with fine interpenetrating networks of ceramics and intermetallics. TiAl (γ) + Ti_3Al (α) lamellar structure led to the enhancement of the mechanical properties.

Reinforced with Al_2O_3

Zhong *et al.* (2014) synthesized 1.5 vol% nano Al_2O_3 reinforced AZ31 using disintegrated melt deposition (DMD) followed by hot-extrusion. Extruded microstructures revealed fine grains and particles of nano-alumina aligned with the extruded direction that act as nucleation sites for enhanced recrystallization.

de Castro *et al.* (Castro *et al.*, 2019) synthesized 10 vol% Al_2O_3 reinforced Mg machining chips using high pressure torsion (HPT). Chips of hard phase Mg slide along Al_2O_3 particles and the composite consists of smaller crystallite size that improved hardness and exhibits greater resistance against creep at room temperature.

Srivastava *et al.* (Srivastava and Chaudhari, 2018) studied the evolution of microstructure of Al6061- nano Al_2O_3 synthesized using ultrasound solidification technique. Al_2O_3 dispersed uniformly in the melt due to intense ultrasonic vibrations. Pure Al_2O_3 alloy fractured due to its dendritic structure and the presence of micro-porosities but the composites exhibited mixed mode fracture with no presence of any particle debonding characteristics.

Reinforced with MgO

Goh *et al.* (2007) studied the addition of nanosized MgO reinforced Mg composites using disintegrated melt deposition (DMD) technique. TEM studies on these composites revealed enhanced interfacial integrity between the matrix and the reinforcement.

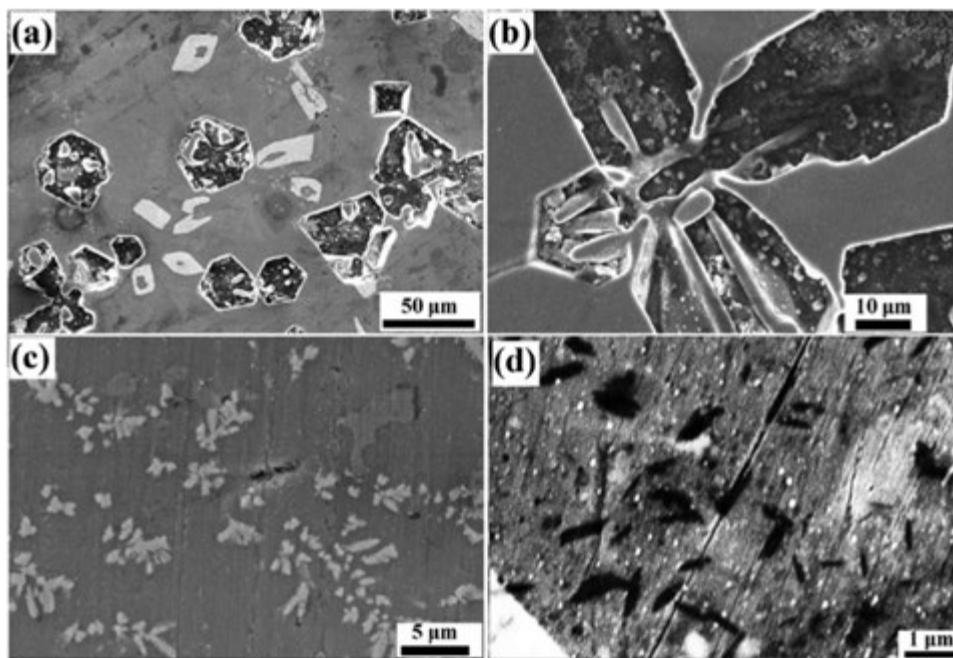


Fig. 17 Microstructural evolution of AE44 matrix composites fabricated by in-situ processing (a) dispersion of coarsened Mg_2Si crystals and Al_xRE_y intermetallics (b) dendritic morphology of Mg_2Si crystal (c) dispersion of fine-sized Al_xRE_y intermetallics and (d) dispersion of fine-sized SiCNO particles. From Chelliah, N.M., Singh, H., Surappa, M.K., 2017. Microstructural evolution and strengthening behavior in in-situ magnesium matrix composites fabricated by solidification processing. *Materials Chemistry and Physics*. 194, 65–76. doi:10.1016/j.matchemphys.2017.03.025.

Cai *et al.* (2018) synthesized Mg-MgO nanocomposites using reactive cryomilling and high pressure consolidation method. These nanocomposites were thermally stable due to strong Zener pinning effect of the in-situ formed MgO nanoparticles located at the grain boundaries with the matrix.

Reinforced with SiC

Saravanan *et al.* (Saravanan and Surappa, 2000) synthesized Mg-30 vol% SiC using melt stir process. SiC particles led to the formation of cellular-dendritic interface in the composite as compared to a typical dendritic structure for pure Mg.

Reinforced with Y_2O_3

Han *et al.* (Han and Dunand, 2000) studied yttria reinforced dispersion strengthened magnesium. Zener pinning of yttria led to reduction in grain sizes of extruded materials to 0.88 μm . Hassan *et al.* (Hassan, 2011) synthesized nano-yttria reinforced magnesium nanocomposites using both blend-press-sinter powder metallurgy process and disintegrated melt deposition (DMD) technique followed by extrusion at increased temperatures. With increase in Y_2O_3 particulates, the volume fraction of recrystallized grains also increased. The nano- Y_2O_3 particulates undergoes pinning the recrystallized magnesium grains leading to its restricted growth.

Reinforced with ZrO_2

Hassan *et al.* (2007) developed nano-zirconia reinforced magnesium nanocomposites using blend-press-sinter powder metallurgy process. Results showed significant grain refinement with minimal porosity post hot-extrusion.

Reinforced with CNTs

Xiang *et al.* (2019) constructed CNTs/Mg laminated composite structure by using electrophoretic deposition technique combined with hot press sintering and hot rolling to generate a micro-nano layered structure. The CNT layers cause high back stress that prevent dislocation slip and hinder the crack propagation.

Titanium Metal Matrix Composites (TMMC)

TMMCs are good candidates for aerospace applications (Liu *et al.*, 2006), for its enhanced oxidation resistance, excellent strength-to-weight ratio and high temperature applicability. Different reinforcements include discontinuous type such as TiB whiskers (Ravi Chandran *et al.*, 2004; Morsi and Patel, 2007), TiC (Geng *et al.*, 2008), TiN (Suárez-Martínez *et al.*, 2020), B_4C (Nartu *et al.*, 2020), graphene (Cao and Liang, 2020), TiB_2 (Liu *et al.*, 2020a), SiC (Liu *et al.*, 2020b), etc. synthesized either using powder metallurgy (in-situ or ex-situ) route or rapid solidification method as ingot metallurgy is not permissible for highly reactive titanium (Hayat *et al.*, 2019).

Several methods such as physical vapor deposition (Lobley and Guo, 1999), tape casting (Lobley and Quo, 1998), induction plasma deposition (Pank and Jackson, 1993) can be used for continuous (fiber) type reinforcements.

Bejjani *et al.* (2016) studied the adiabatic shear bands (ASB) produced in segmented chips of Ti-MMCs when they are subjected to machining. During the formation of chip, dynamic recovery takes place and the large grains containing high-energy configurational dislocations leads to its rearrangement within elongated cells. With increase in misorientations, subgrain boundaries evolve and leads to evolution of nanograin structure.

Ozerov *et al.* (2019) studied the microstructural evolution during multiaxial forging (MAF) of Ti/TiB MMC produced due to spark plasma sintering (SPS) process. Ti and TiB₂ reacted to form TiB whiskers. Dynamic recrystallization occurred during forging at 700–850°C leads to dislocation free recrystallized areas and shortened TiB whiskers.

Kim *et al.* (Kim and Choi, 2004) studied the microstructural influences and process conditions on consolidation behavior of SiC fiber/Ti-6Al-4V foil MMCs. At a consolidation pressure of 30 MPa at 900°C, it exhibited a heterogeneous microstructure consisting equiaxed α , widmanstätten α and transformed β . Different geometrical arrangements of foil-fiber-foil type can lead to different levels of densification and hence the mechanical properties.

Vancheeswaran *et al.* (1997) developed a consolidation path planning simulations to arrive at pre-determined microstructure of a fiber reinforced composite. A micromechanical model consisting of local linear approximations was chosen to achieve enhanced mechanical performance for Ti-6Al-4V/SCS-6 composite.

Li *et al.* (2017) used selective laser melting technique to study the phase transformation and texture evolution of TiAl/TiB₂ in-situ MMCs that exhibited enhanced nanohardness. The microstructure consisted of α_2 (Ti₃Al), γ (TiAl), B₂, TiB₂ and TiB phases. With increase in TiB₂ content, refined grain structure was observed. It also led to texture strengthening of basal ($\{0001\} <11\bar{2}0>$), prismatic ($\{10\bar{1}0\} <11\bar{2}0>$) and pyramidal fibers ($\{10\bar{1}1\} <11\bar{2}0>$ and $\{11\bar{2}2\} <11\bar{2}3>$) of Ti₃Al phase.

Guo *et al.* (2012) studied reaction between Ti and LaB₆ to synthesize TiB whiskers and La₂O₃ reinforced Ti MMCs synthesized using vacuum arc remelting process, followed by hot rolling. Increased deformation degree led to rotation of whiskers that contributed in enhancement of room-temperature tensile properties.

Hybrid Metal Matrix Composites

Hybrid reinforcements onto MMCs develop synergistic effects and exhibit significant improvement in the properties compared to their counterparts. Zhou *et al.* reviewed progress in hybrid MMCs (Zhou *et al.*, 2020). They discussed common reinforcements used in MMCs. Among continuous reinforcement type, fibers of C, SiC, Al₂O₃, B and wires of steel and W can be used (Zhou *et al.*, 2020). Among discontinuous type, ceramic particles like SiC, Al₂O₃, B₄C, TiB₂, AlN etc., metallic particles like Ti, Cu, Ni, Zr etc., are used. Zhou *et al.* also synthesized micron SiC and CNT reinforced AZ61 alloy composites using powder metallurgy followed by hot-extrusion (Zhou *et al.*, 2019). The novel multi-dispersion process for homogeneous dispersion consisted of CNT adsorption onto SiC surface via hydrogen bonding followed by ball milling.

Li *et al.* (2015) studied the synergistic strengthening effect by preparing Al MMC made of reduced graphene oxide (RGO) and carbon nanotube (CNT), whose planar network led to increased load transfer among the constituents.

Wei *et al.* (2018) fabricated network Ti-6Al-4V/(TiB + TiC) hybrid composites prepared using reaction hot pressing technique exhibits enhanced cyclic oxidation resistance. The reinforcement phases exhibit a 3D network microstructure within bulk composite as seen in Fig. 18, where TiC particles and TiB whiskers are selectively distributed on the Ti-6Al-4V intergranular boundaries. The reinforcement led to the change in the internal microstructure from Widmanstätten lamellae to α -Ti equi-axed grains.

Texture

It is not only the changes in microstructure that influences the material properties, but it is also highly dependent on texture. The processing route decides the texture of the composite, which can influence several properties (Suresh *et al.*, 2013). Texture formation takes place via phase transformation, recrystallization, plastic deformation, etc. (Kestens and Pircgazi, 2016). Secondary processes such as extrusion causes directional alignment of the grains, phases and breaks down the reinforcements and aligns them parallel to streamlines. Sometimes the amount of reinforcement material can enhance the texture, as seen by Li *et al.* (2017) where texture strength of TiAl/TiB₂ in-situ MMCs increased with the amount of TiB₂. Shahani *et al.* (Shahani and Clyne, 1991) studied Al₂O₃ dispersed in Al and found strong texture in the matrix for spherical particle reinforcement and observed weakened texture with increase in aspect ratio. Nucleation enhanced with increasing volume fraction of the particles and among them, large particles stimulate nucleation and fine oxide particles inhibited.

Cold-Rolling Texture

Dan *et al.* (2018) using neutron diffraction and EBSD analysis studied the cold rolling texture evolution of TiB₂ reinforced Al composites. The reinforcement influenced the texture in two different ways, the non-shearable and small TiB₂ particles contributed to dominant $\{112\} <111>$ copper orientation at high strains whereas the clusters of TiB₂ along the grain boundaries and the

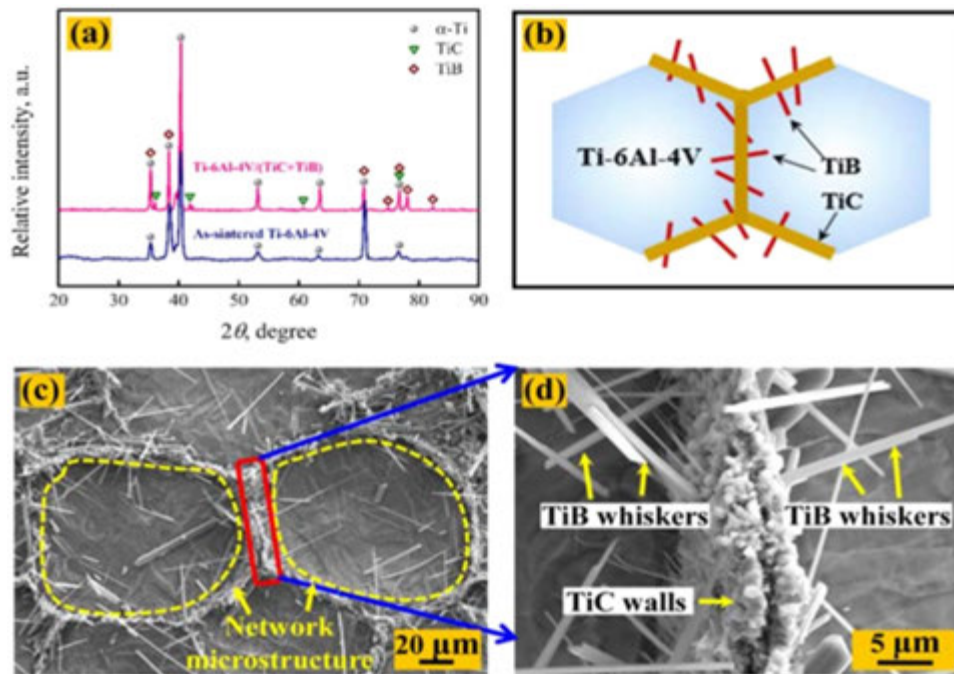


Fig. 18 (a) XRD patterns of typical Ti-6Al-4V/(TiC + TiB) composites and as-sintered Ti-6Al-4V, (b) Ideal network microstructure designed for Ti-6Al-4V/(TiC + TiB) composites, (c,d) SEM micrographs. From Wei, S.L., *et al.*, 2018. Interactive effects of cyclic oxidation and structural evolution for Ti-6Al-4V/(TiC + TiB) alloy composites at elevated temperatures. *Journal of Alloys and Compounds*. 752, 164–178. doi:[10.1016/j.jallcom.2018.04.118](https://doi.org/10.1016/j.jallcom.2018.04.118).

recrystallized nuclei led to weak texture. The regions around these clusters was called particle deformed zone and some cube {001} <100> orientations were observed.

Recrystallization Texture

Poudens *et al.* (Poudens and Bacroix, 1996) studied the recrystallization textures in Al-SiC MMCs after subjected to a deformation process. Particle stimulated nucleation (PSN) process creates distorted zones of heterogeneous deformation that yields weak textures, barring small sized shearable particles that result in a strong texture and it is attributed to the shear bands caused during deformation (Lücke and Engler, 1990).

Aging Kinetics of Particle Reinforced Aluminum Metal Matrix Composites

The composite matrix exhibits enhanced dislocation densities due to the presence of reinforcements. Suresh *et al.* (1989) observed accelerated aging in Al-Cu-SiC particulated composites and this phenomenon did not enhance with increase in reinforcement addition. SiC enhances the precipitation kinetics of the composite material in comparison with the material without reinforcement. The dislocation densities are found to be greater at the particle/matrix interface, where the hardening phenomenon was observed to faster by Dutta *et al.* (Dutta and Surappa, 1997) during their studies on the age-hardening characteristics of Al-Cu-SiCp composites and it slows with increasing distance. After the samples are subjected to solutionizing temperature, thermal residual stresses evolve when they are cooled to room temperature before aging. Precipitate nucleation and growth is a function of matrix dislocation density distributions (Dutta and Bourell, 1990) and several models have been proposed in this regard.

Microstructural aspects of age-hardening precipitation reactions in SiC whiskers and particles reinforced Al MMCs using Differential Scanning Calorimeter (DSC) was carried out by Papazian (1988). This method is rapid and precipitation reactions can be detected corresponding to change in enthalpies. The cold rolling effect on aging kinetics of alumina reinforced AA6061 composites was studied by Lee *et al.* (1991) using DSC. Similar to reinforcement addition, it was found that cold rolling produced an increased dislocation density that caused accelerated aging. Christman *et al.* (Christman and Suresh, 1988) studied changes in electrical conductivity behavior to interpret the microstructural aspects of SiC whisker reinforced Al MMCs. As the reinforcement material here is an excellent electron scatterer, the composite exhibited lower conductivity compared to the base alloy (AA2124). During the aging process, the normalized conductivity values of the base alloy and the composite did not vary to a greater extent, except in the beginning where the rate of conductivity declining was greater for the composite than the base alloy.

Corrosion

Imeson *et al.* (Imeson and Bartlett, 1995) linked corrosion phenomenon to the microstructure of SiC reinforced AA2124 MMC directly using TEM. Samples were subjected to a “flash corrosion” etching treatment prior to TEM examination. It was found that the SiC particles and intermetallic precipitates did not have a major role in pit initiation, but the microstructural features comprising of Mg segregation close to SiC interfaces and Mg₂Si was the primary cause.

Study of Interfaces and Interlayers

Thermal Mismatch

Vogelsang *et al.* (1986) used a High Voltage Electron Microscope (HVEM) to study the dislocation generation at the Al/(discontinuous or platlet type SiC) interfaces during cooling after annealing treatment. This was attributed to the high difference in thermal expansion coefficients of Al and SiC that strengthens the composite due to high density of dislocations. Chawla *et al.* (Chawla and Metzger, 1972) investigated the microstructure of W-fiber reinforced Cu composites using dislocation etch pitting technique. They accounted for transverse and axial strains due to the differential shrinkage and also studied the interface shear.

Qu *et al.* (2011) reviewed the thermo-physical properties of MMCs like SiC/metal, C/metal, diamond/metal for thermal management applications. In the case of SiC/Al and C/Al composites, the formation of Al₄C₃ due to interfacial reaction (Etter *et al.*, 2007; Ren *et al.*, 2008) can degrade thermal properties. For SiC/Cu composites, the formation of Cu₃Si influences the reactive wetting (Rado *et al.*, 2000) and hence the thermal properties. Addition of Ti can enhance wettability between SiC and Cu (Krauß *et al.*, 2002). Several studies on the thermal conductivity of diamond reinforced MMCs (Shao *et al.*, 2004; Beffort *et al.*, 2006; Weber and Tavangar, 2007; Molina *et al.*, 2008; Mizuuchi *et al.*, 2010; Dong *et al.*, 2011) shows the importance of interface structure for improved bonding.

Conclusion

Structural factors like periodicity of phase components, phase dimensions, their geometric arrangement, volume fraction and processing conditions are important factors in deciding the final properties of the composites. Interaction between the matrix and reinforcement, and the interface engineering needs to be further understood for a wide range of materials. Metal matrix composites can be synthesized using different processes and hence different microstructures can be achieved. Tailoring these microstructures helps a materials scientist to enhance the performance of the composite developed for a specific application, which the conventional material is not capable of delivering it. Composite materials is a rapidly developing field and with rising socio-economic standards in many countries, this will have a lucrative growth estimated in the coming future.

References

- Abbas, A., Huang, S.J., 2020. ECAP effects on microstructure and mechanical behavior of annealed WS₂/AZ91 metal matrix composite. *Journal of Alloys and Compounds* 835. 155466. doi:10.1016/j.jallcom.2020.155466.
- Agarwal, A., Bakshi, S.R., Lahiri, D., 2016. Carbon Nanotubes: Reinforced Metal Matrix Composites. CRC Press.
- Aherwar, A., Patnaik, A., Pruncu, C.I., 2020. Effect of B4C and waste porcelain ceramic particulate reinforcements on mechanical and tribological characteristics of high strength AA7075 based hybrid composite. *Journal of Materials Research and Technology*. 9 (5), 9882–9894. doi:10.1016/j.jmrt.2020.07.003.
- Anthony Xavier, M., Prashantha Kumar, H.G., 2017. Processing and characterization techniques of graphene reinforced metal matrix composites (GRMMC); A review. In: Bland, S. (Ed.), *Materials Today: Proceedings*. Elsevier, pp. 3334–3341. doi:10.1016/j.matpr.2017.02.220.
- Aristizabal, K., *et al.*, 2020. Microstructural evolution during heating of CNT/metal matrix composites processed by severe plastic deformation. *Scientific Reports* 10 (1), 1–10. doi:10.1038/s41598-020-57946-3.
- Arsenault, R.J., *et al.*, 1991. Localized deformation of SiC/Al composites. *Materials Science and Engineering A* 131 (1), 55–68. doi:10.1016/0921-5093(91)90344-M.
- Ashby, M.F., 2001. Composite materials, Microstructural design of. In: Jürgen Buschow, K.H., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*, second ed. Elsevier, pp. 1357–1361. doi:10.1016/B0-08-043152-6/00253-9.
- Asthana, R., Tewari, S.N., 1993. The engulfment of foreign particles by a freezing interface. *Journal of Materials Science*. 5414–5425. doi:10.1007/BF00367810.
- Baker, A.A., Shipman, M.C., Jackson, P.W., 1972. The short-term compatibility of carbon fibres with aluminium. *Fibre Science and Technology* 5 (3), 213–218. doi:10.1016/0015-0568(72)90016-4.
- Basak, A.K., Pramanik, A., Prakash, C., 2019. Deformation and strengthening of SiC reinforced Al-MMCs during in-situ micro-pillar compression. *Materials Science and Engineering A* 763. 138141. doi:10.1016/j.msea.2019.138141.
- Batista, L.A., *et al.*, 2019. Influence of multi-walled carbon nanotubes reinforcements on hardness and abrasion behaviour of porous Al-matrix composite processed by cold pressing and sintering. *Journal of Alloys and Compounds* 791, 96–99. doi:10.1016/j.jallcom.2019.03.265.
- Bauri, R., Yadav, D., Nishida, Y., 2018. Introduction to metal matrix composites. In: *Metal Matrix Composites by Friction Stir Processing*. Butterworth-Heinemann. doi:10.1016/b978-0-12-813729-1.00001-2.
- Beffort, O., *et al.*, 2006. Interface formation in infiltrated Al(Si)/diamond composites. In: Haenen, K. (Ed.), *Diamond and Related Materials* 15. Elsevier, pp. 1250–1260. doi:10.1016/j.diamond.2005.09.036.
- Bejjani, R., *et al.*, 2016. Chip formation and microstructure evolution in the adiabatic shear band when machining titanium metal matrix composites. *International Journal of Machine Tools and Manufacture* 109, 137–146. doi:10.1016/j.ijmachtools.2016.08.001.

- Bommala, V.K., Krishna, M.G., Rao, C.T., 2019. Magnesium matrix composites for biomedical applications: A review. *Journal of Magnesium and Alloys*. 72–79. doi:10.1016/j.jma.2018.11.001.
- Cai, X., *et al.*, 2018. Thermally stable and strong bulk Mg–MgO in situ nanocomposites by reactive cryomilling and high-pressure consolidation. *Journal of Materials Science* 53 (9), 6613–6625. doi:10.1007/s10853-018-2041-x.
- Cao, H.C., Liang, Y.L., 2020. The microstructures and mechanical properties of graphene-reinforced titanium matrix composites. *Journal of Alloys and Compounds* 812. 152057. doi:10.1016/j.jallcom.2019.152057.
- Cao, L., *et al.*, 1990. Study of the whisker rotation in metal matrix composite. *Composites* 21 (2), 127–131. doi:10.1016/0010-4361(90)90004-G.
- Castro, M.M., *et al.*, 2019. Development of a magnesium-alumina composite through cold consolidation of machining chips by high-pressure torsion. *Journal of Alloys and Compounds* 780, 422–427. doi:10.1016/j.jallcom.2018.11.357.
- Chang, H., *et al.*, 2012. Microstructure and mechanical properties of the Mg/Al multilayer fabricated by accumulative roll bonding (ARB) at ambient temperature. *Materials Science and Engineering A* 543, 249–256. doi:10.1016/j.msea.2012.02.083.
- Chang, Y., *et al.*, 2019. Continuous Mo fiber reinforced Ti/Al₃Ti metal-intermetallic laminated composites. *Intermetallics* 112, 106544. doi:10.1016/j.intermet.2019.106544.
- Chaubey, A.K., *et al.*, 2012. Effect of particle dispersion on the mechanical behavior of Al-based metal matrix composites reinforced with nanocrystalline Al–Ca intermetallics. *Journal of Alloys and Compounds*. S134–S137. doi:10.1016/j.jallcom.2011.12.075.
- Chawla, K.K., Metzger, M., 1972. Initial dislocation distributions in tungsten fibre-copper composites. *Journal of Materials Science* 7 (1), 34–39. doi:10.1007/BF00549547.
- Chelliah, N.M., Singh, H., Surappa, M.K., 2017. Microstructural evolution and strengthening behavior in in-situ magnesium matrix composites fabricated by solidification processing. *Materials Chemistry and Physics* 194, 65–76. doi:10.1016/j.matchemphys.2017.03.025.
- Chen, B., *et al.*, 2020a. Microstructure, tensile properties and deformation behaviors of aluminium metal matrix composites co-reinforced by ex-situ carbon nanotubes and in-situ alumina nanoparticles. *Materials Science and Engineering: A*. 139930. doi:10.1016/j.msea.2020.139930.
- Chen, F., *et al.*, 2020b. Tribological behavior and mechanism of h-BN modified copper metal matrix composites paired with C/C–SiC. *Tribology International* 153. 106561doi:10.1016/j.triboint.2020.106561.
- Chen, L., *et al.*, 2020c. In situ TiC/Inconel 625 nanocomposites fabricated by selective laser melting: densification behavior, microstructure evolution, and wear properties. *Applied Surface Science* 518, 145981. doi:10.1016/j.apsusc.2020.145981.
- Chen, Z.J., *et al.*, 2015. Deformation inhomogeneities of Mg–Al laminated metal composites fabricated by accumulative roll bonding. *Materials Research Innovations* 19, S147–S151. doi:10.1179/1432891715Z.0000000001533.
- Chen, Z.-G., *et al.*, 2009. Microstructural evolution and its effects on mechanical properties of spray deposited SiCp/8009Al composites during secondary processing. *Transactions of Nonferrous Metals Society of China* 19 (5), 1116–1120. doi:10.1016/S1003-6326(08)60416-1.
- Chidambaram, A., Bhole, S.D., 1997. Metallographic preparation of aluminum-alumina metal-matrix composites. *Materials Characterization* 38 (3), 187–191. doi:10.1016/S1044-5803(97)00041-7.
- Christman, T., Suresh, S., 1988. Microstructural development in an aluminum alloy–SiC whisker composite. *Acta Metallurgica* 36 (7), 1691–1704. doi:10.1016/0001-6160(88)90236-2.
- Chun, H.J., Daniel, I.M., 1997. Transverse creep behavior of a unidirectional metal matrix composite. *Mechanics of Materials* 25 (1), 37–46. doi:10.1016/S0167-6636(96)00049-X.
- Dan, C.Y., *et al.*, 2018. Cold rolling texture evolution of TiB₂ particle reinforced Al-based composites by neutron diffraction and EBSD analysis. *Materials Characterization* 136, 293–301. doi:10.1016/j.matchar.2017.12.028.
- Dele-Afolabi, T.T., *et al.*, 2018. Significant effect of rice husk and sugarcane bagasse pore formers on the microstructure and mechanical properties of porous Al₂O₃/Ni composites. *Journal of Alloys and Compounds* 743, 323–331. doi:10.1016/j.jallcom.2018.01.230.
- Deng, K.K., *et al.*, 2010. Microstructure evolution and mechanical properties of a particulate reinforced magnesium matrix composites forged at elevated temperatures. *Materials Science and Engineering A* 527 (6), 1630–1635. doi:10.1016/j.msea.2009.10.053.
- Derby, B., Wallach, E.R., 1984. Diffusion bonding: Development of theoretical model. *Metal Science* 18 (9), 427–431. doi:10.1179/030634584790419809.
- Dermarkar, S., Chawla, N., Chawla, K.K., 2006. In: Kainer, K.U. (Ed.), *Metal Matrix Composites, Metals and Materials* (Institute of Metals). Springer Science + Business Media, INC.
- Ding, X.D., *et al.*, 2002. Stress-strain behavior in initial yield stage of short fiber reinforced metal matrix composite. *Composites Science and Technology* 62 (6), 841–850. doi:10.1016/S0266-3538(02)00024-6.
- Dong, Y.H., *et al.*, 2011. Fabrication and thermal conductivity of near-net-shaped diamond/copper composites by pressureless infiltration. *Journal of Materials Science* 46 (11), 3862–3867. doi:10.1007/s10853-011-5307-0.
- Dutta, B., Surappa, M.K., 1997. Studies on age-hardening characteristics of ceramic particle/matrix interfaces in Al–Cu–SiCp composites using ultra low-load-dynamic microhardness measurements. *Journal of Materials* 12 (10), 2773–2778. doi:10.1557/JMR.1997.0369.
- Dutta, B., Surappa, M.K., 1998. Directional dendritic solidification of a composite slurry: Part I. Dendrite morphology. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science* 29 (4), 1319–1327. doi:10.1007/s11661-998-0258-z.
- Dutta, I., 2000. Role of interfacial and matrix creep during thermal cycling of continuous fiber reinforced metal-matrix composites. *Acta Materialia* 48 (5), 1055–1074. doi:10.1016/S1359-6454(99)00402-4.
- Dutta, I., Bourell, D.L., 1990. Influence of dislocation density and distribution on the aging behavior of 6061 AlSiCw composites. *Acta Metallurgica Et Materialia* 38 (11), 2041–2049. doi:10.1016/0956-7151(90)90071-N.
- Eter, T., *et al.*, 2007. Aluminium carbide formation in interpenetrating graphite/aluminium composites. *Materials Science and Engineering A*. 1–6. doi:10.1016/j.msea.2006.11.088.
- Everett, R., Arsenault, R., 1991. *Metal Matrix Composites: Processing and Interfaces*. Academic Press. doi:10.1016/b978-0-12-341832-6.x5001-4.
- Ganesh, V.V., Chawla, N., 2005. Effect of particle orientation anisotropy on the tensile behavior of metal matrix composites: experiments and microstructure-based simulation. *Materials Science and Engineering A* 391 (1–2), 342–353. doi:10.1016/j.msea.2004.09.017.
- Geng, L., *et al.*, 2008. Hybrid effect of TiBw and TiCp on tensile properties of in situ titanium matrix composites. *Journal of Alloys and Compounds* 463 (1–2), 488–492. doi:10.1016/j.jallcom.2007.09.054.
- Ghasali, E., *et al.*, 2019. Corrosion behavior and in-vitro bioactivity of porous Mg/Al₂O₃ and Mg/Si₃N₄ metal matrix composites fabricated using microwave sintering process. *Materials Chemistry and Physics* 225, 331–339. doi:10.1016/j.matchemphys.2019.01.007.
- Goh, C.S., *et al.*, 2007. Characterization of high performance Mg/MgO nanocomposites. *Journal of Composite Materials* 41 (19), 2325–2335. doi:10.1177/0021998307075445.
- Guo, X., *et al.*, 2012. Effects of degree of deformation on the microstructure, mechanical properties and texture of hybrid-reinforced titanium matrix composites. *Acta Materialia* 60 (6–7), 2656–2667. doi:10.1016/j.actamat.2012.01.032.
- Guo, Z.X., Derby, B., 1993. Microstructural characterization in diffusion-bonded SiC/Ti–6Al–4V composites. *Journal of Microscopy* 169 (2), 269–277. doi:10.1111/j.1365-2818.1993.tb03304.x.
- Gupta, M., Sharon, N.M.L., 2010. *Magnesium, Magnesium Alloys, and Magnesium Composites*. Wiley. doi:10.1002/9780470905098.
- Habila, W., *et al.*, 2019. Investigation of microstructure and texture evolution of a Mg/Al laminated composite elaborated by accumulative roll bonding. *Materials Characterization* 147, 242–252. doi:10.1016/j.matchar.2018.11.010.
- Han, B.Q., Dunand, D.C., 2000. Microstructure and mechanical properties of magnesium containing high volume fractions of yttria dispersoids. *Materials Science and Engineering A* 277 (1–2), 297–304. doi:10.1016/S0921-5093(99)00074-x.

- Hashim, J., Looney, L., Hashmi, M.S.J., 2002. Particle distribution in cast metal matrix composites - Part I. *Journal of Materials Processing Technology* 123 (2), 251–257. doi:10.1016/S0924-0136(02)00098-5.
- Hassan, S.F., 2011. Effect of primary processing techniques on the microstructure and mechanical properties of nano-Y₂O₃ reinforced magnesium nanocomposites. *Materials Science and Engineering A* 528 (16–17), 5484–5490. doi:10.1016/j.msea.2011.03.063.
- Hassan, S.F., Tan, M.J., Gupta, M., 2007. Development of nano-ZrO₂ reinforced magnesium nanocomposites with significantly improved ductility. *Materials Science and Technology*. 1309–1312. doi:10.1179/174328407 × 236913.
- Hayat, M.D., *et al.*, 2019. Titanium metal matrix composites: An overview. *Composites Part A: Applied Science and Manufacturing* 121 (April), 418–438. doi:10.1016/j.compositesa.2019.04.005.
- He, C.N., *et al.*, 2009. Mechanical properties and microstructures of carbon nanotube-reinforced Al matrix composite fabricated by in situ chemical vapor deposition. *Journal of Alloys and Compounds* 487 (1–2), 258–262. doi:10.1016/j.jallcom.2009.07.099.
- He, P., *et al.*, 2003. A new technology for diffusion bonding intermetallic TiAl to steel with composite barrier layers. *Materials Characterization* 50 (1), 87–92. doi:10.1016/S1044-5803(03)00122-0.
- Horvitz, D., Gotman, I., 2002. Pressure-assisted SHS synthesis of MgAl₂O₄-TiAl in situ composites with interpenetrating networks. *Acta Materialia* 50 (8), 1961–1971. doi:10.1016/S1359-6454(02)00041-1.
- Hoseini Athar, M.M., Tolaminejad, B., 2015. Weldability window and the effect of interface morphology on the properties of Al/Cu/Al laminated composites fabricated by explosive welding. *Materials and Design* 86, 516–525. doi:10.1016/j.matdes.2015.07.114.
- Hu, K., *et al.*, 2018. Effects of nano-SiCp content on microstructure and mechanical properties of SiCp/A356 composites assisted with ultrasonic treatment. *Transactions of Nonferrous Metals Society of China* 28 (11), 2173–2180. doi:10.1016/S1003-6326(18)64862-9.
- Hu, Y., *et al.*, 2020. Microstructure characteristics of a high-entropy-alloy intermetallic laminate composite. *Materials Letters* 273. 127937. doi:10.1016/j.matlet.2020.127937.
- Huang, G., Hou, W., Shen, Y., 2018. Evaluation of the microstructure and mechanical properties of WC particle reinforced aluminum matrix composites fabricated by friction stir processing. *Materials Characterization* 138, 26–37. doi:10.1016/j.matchar.2018.01.053.
- Ibrahim, I.A., Mohamed, F.A., Lavernia, E.J., 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science*. 1137–1156. doi:10.1007/BF00544448.
- Imeson, D., Bartlett, D.L., 1995. Microstructural origins of corrosion in a 20% SiCp/2124 aluminium alloy metal matrix composite. *Journal of Microscopy* 177 (3), 347–356. doi:10.1111/j.1365-2818.1995.tb03566.x.
- Ivanov, D., *et al.*, 2017. Evolution of structure and properties of the nickel-based alloy EP718 after the SLM growth and after different types of heat and mechanical treatment. *Additive Manufacturing* 18, 269–275. doi:10.1016/j.addma.2017.10.015.
- Jackson, P.W., Braddick, D.M., Walker, P.J., 1972. Tensile and flexural properties of carbon fibre-aluminium matrix composites. *Fibre Science and Technology* 5 (3), 219–236. doi:10.1016/0015-0568(72)90017-6.
- Kawasaki, M., *et al.*, 2016. Using high-pressure torsion to process an aluminum-magnesium nanocomposite through diffusion bonding. *Journal of Materials Research* 31 (1), 88–99. doi:10.1557/jmr.2015.257.
- Kelen, F., Gavali, M., Aydogmus, T., 2018. Microstructure and mechanical properties of a novel TiNi particulate reinforced AZ91 metal matrix composite. *Materials Letters* 233, 12–15. doi:10.1016/j.matlet.2018.08.121.
- Kestens, L.A.I., Pirgazi, H., 2016. Texture formation in metal alloys with cubic crystal structures. *Materials Science and Technology* 32, 1303–1315. doi:10.1080/02670836.2016.1231746.
- Khorasani, A.M., *et al.*, 2019. The effect of SLM process parameters on density, hardness, tensile strength and surface quality of Ti-6Al-4V. *Additive Manufacturing* 25, 176–186. doi:10.1016/j.addma.2018.09.002.
- Kim, H.G., 2008. Effects of fiber aspect ratio evaluated by elastic analysis in discontinuous composites. *Journal of Mechanical Science and Technology* 22 (3), 411–419. doi:10.1007/s12206-007-1208-1.
- Kim, T.W., Choi, N.S., 2004. Microstructural influences on consolidation behavior of titanium metal matrix composites. *Materials Science and Engineering A* 387–389 (1–2 SPEC. ISS.), 887–891. doi:10.1016/j.msea.2003.12.091.
- Krauß, G., Kübler, J., Trentini, E., 2002. Preparation and properties of pressureless infiltrated SiC and AlN particulate reinforced metal ceramic composites based on bronze and iron alloys. *Materials Science and Engineering A* 337 (1–2), 315–322. doi:10.1016/S0921-5093(02)00044-8.
- Kundu, P., Kundu, S., Mishra, A., 2013. Microstructure Analysis of Aluminium metal matrix alloy with Silicon Carbide. *International Journal of Current Engineering and Technology* 3 (5), 2167–2170. Available at: <http://inpressco.com/category/ijcet>.
- Kurumlu, D., *et al.*, 2012. On the presence of work-hardened zones around fibers in a short-fiber-reinforced Al metal matrix composite. *Acta Materialia* 60 (17), 6051–6064. doi:10.1016/j.actamat.2012.07.042.
- Lee, H.L., Lu, W.H., Chan, S.L.I., 1991. Effect of cold rolling on the aging kinetics of Al₂O₃ 6061 Al composite by differential scanning calorimetric technique. *Scripta Metallurgica Et Materialia* 25 (9), 2165–2170. doi:10.1016/0956-716X(91)90293-A.
- Lee, I.S., Kao, P.W., Ho, N.J., 2008. Microstructure and mechanical properties of Al-Fe in situ nanocomposite produced by friction stir processing. *Intermetallics* 16 (9), 1104–1108. doi:10.1016/j.intermet.2008.06.017.
- Lee, Y.H., *et al.*, 2020. Microstructure and mechanical properties of lightweight TiC-steel composite prepared by liquid pressing infiltration process. *Materials Characterization* 162. 110202doi:10.1016/j.matchar.2020.110202.
- Li, H., *et al.*, 2020. Microstructure evolution and mechanical properties of selective laser melted bulk-form titanium matrix nanocomposites with minor B4C additions. *Materials and Design* 185. 108245doi:10.1016/j.matdes.2019.108245.
- Li, W., *et al.*, 2017. Enhanced nanohardness and new insights into texture evolution and phase transformation of TiAl/TiB₂ in-situ metal matrix composites prepared via selective laser melting. *Acta Materialia* 136, 90–104. doi:10.1016/j.actamat.2017.07.003.
- Li, Z., *et al.*, 2015. Synergistic strengthening effect of graphene-carbon nanotube hybrid structure in aluminum matrix composites. *Carbon* 95, 419–427. doi:10.1016/j.carbon.2015.08.014.
- Liu, H.S., Zhang, B., Zhang, G.P., 2011. Microstructures and mechanical properties of Al/Mg alloy multilayered composites produced by accumulative roll bonding. *Journal of Materials Science and Technology* 27 (1), 15–21. doi:10.1016/S1005-0302(11)60019-4.
- Liu, L., *et al.*, 2020a. Selective laser melting of TiB₂-Ti composite with high content of ceramic phase. *Ceramics International* 46 (13), 21128–21135. doi:10.1016/j.ceramint.2020.05.189.
- Liu, Y., *et al.*, 2020b. Microstructure and mechanical properties of SiC nanowires reinforced titanium matrix composites. *Journal of Alloys and Compounds* 819. 152953doi:10.1016/j.jallcom.2019.152953.
- Liu, X., *et al.*, 2017. The role of ultrasound in hydrogen removal and microstructure refinement by ultrasonic argon degassing process. *Ultrasonics Sonochemistry* 38, 455–462. doi:10.1016/j.ulsonch.2017.03.041.
- Liu, X.B., Chen, R.S., Han, E.H., 2009. Preliminary investigations on the Mg-Al-Zn/Al laminated composite fabricated by equal channel angular extrusion. *Journal of Materials Processing Technology* 209 (10), 4675–4681. doi:10.1016/j.jmatprotec.2008.11.034.
- Liu, Y., *et al.*, 2006. Design of powder metallurgy titanium alloys and composites. *Materials Science and Engineering A* 418 (1–2), 25–35. doi:10.1016/j.msea.2005.10.057.
- Lloyd, D.J., 1991. Aspects of fracture in particulate reinforced metal matrix composites. *Acta Metallurgica Et Materialia* 39 (1), 59–71. doi:10.1016/0956-7151(91)90328-X.
- Lobley, C.M., Quo, Z.X., 1998. Processing of Ti-SiC metal matrix composites by tape casting. *Materials Science and Technology* 14 (9–10), 1024–1028. doi:10.1179/mst.1998.14.9-10.1024.

- Lobley, C.M., Guo, Z.X., 1999. Viable routes to large-scale commercialisation of silicon carbide fibre titanium matrix composites. *Materials*. 133–138. doi:10.1080/10667857.1999.11752829.
- Lücke, K., Engler, O., 1990. Effects of particles on development of microstructure and texture during rolling and recrystallisation in fcc alloys. *Materials Science and Technology* 6 (11), 1113–1130. doi:10.1179/mst.1990.6.11.1113.
- Luo, C., *et al.*, 2013. Effect of high temperature annealing and subsequent hot rolling on microstructural evolution at the bond-interface of Al/Mg/Al alloy laminated composites. *Materials Characterization* 84, 34–40. doi:10.1016/j.matchar.2013.07.007.
- Ma, Y., *et al.*, 2020. Atomic-scale investigation of the interface precipitation in a TiB₂ nanoparticles reinforced Al–Zn–Mg–Cu matrix composite. *Acta Materialia* 185, 287–299. doi:10.1016/j.actamat.2019.11.068.
- Madhusudan, S., Sarcar, M.M.M., Rao, N.B.R.M., 2016. Mechanical properties of Aluminum-Copper(p) composite metallic materials. *Journal of Applied Research and Technology* 14 (5), 293–299. doi:10.1016/j.jart.2016.05.009.
- Magalhães, D.C.C., Sordi, V.L., Kliuga, A.M., 2020. Microstructure evolution of multilayered composite sheets of AA1050/AA7050 Al alloys produced by asymmetric accumulative roll-bonding. *Materials Characterization* 162, 110226. doi:10.1016/j.matchar.2020.110226.
- Manohar, G., *et al.*, 2018. Fabrication of metal matrix composites by powder metallurgy: A review. *AIP Conference Proceedings* 1952, 020041. doi:10.1063/1.5032003.
- McNelly, T.R., Edwards, G.R., Sherby, O.D., 1977. A microstructural correlation between the mechanical behavior of large volume fraction particulate composites at low and high temperatures. *Acta Metallurgica* 25 (2), 117–124. doi:10.1016/0001-6160(77)90115-8.
- McWilliams, B.A., Yen, C.F., 2016. Multi-scale modeling of continuous ceramic fiber reinforced aluminum matrix composites. In: Sano, T., Srivatsan, T.S., Peretti, M.W. (Eds.), *Advanced Composites for Aerospace, Marine, and Land Applications*. Springer, pp. 203–211. doi:10.1007/978-3-319-48096-1_17.
- Meyers, M.A., Wang, S.L., 1988. An improved method for shock consolidation of powders. *Acta Metallurgica* 36 (4), 925–936. doi:10.1016/0001-6160(88)90147-2.
- Mileiko, S.T., Kolchin, A.A., Prokopenko, V.M., 2020. Yttrium-aluminium-perovskite-fibre/molybdenum-matrix composites: strength, fracture toughness and oxidation resistance. *Composites Part B: Engineering* 182, 107604. doi:10.1016/j.compositesb.2019.107604.
- Mizumoto, M., Ohgai, T., Kagawa, A., 2005. Characterization of fiber-reinforced metal matrix composites fabricated by low-pressure infiltration process. *Materials Science and Engineering A* 413–414, 521–526. doi:10.1016/j.msea.2005.07.065.
- Mizuuchi, K., *et al.*, 2010. Thermal properties of diamond-particle-dispersed Cu-matrix-composites fabricated by spark plasma sintering (SPS). *Materials Science Forum*. 2115–2120. doi:10.4028/www.scientific.net/MSF.638-642.2115.
- Molina, J.M., *et al.*, 2008. Thermal conductivity of aluminum matrix composites reinforced with mixtures of diamond and SiC particles. *Scripta Materialia* 58 (5), 393–396. doi:10.1016/j.scriptamat.2007.10.020.
- Morsi, K., Patel, V.V., 2007. Processing and properties of titanium-titanium boride (TiB_w) matrix composites – A review. *Journal of Materials Science*. 2037–2047. doi:10.1007/s10853-006-0776-2.
- Nardone, V.C., Prew, K.M., 1986. On the strength of discontinuous silicon carbide reinforced aluminum composites. *Scripta Metallurgica* 20 (1), 43–48. doi:10.1016/0036-9748(86)90210-3.
- Nartu, M.S.K.K.Y., *et al.*, 2020. In situ reactions during direct laser deposition of Ti-B₄C composites. *Scripta Materialia* 183, 28–32. doi:10.1016/j.scriptamat.2020.03.021.
- Ozerov, M., *et al.*, 2019. Evolution of microstructure and mechanical properties of Ti/TiB metal-matrix composite during isothermal multiaxial forging. *Journal of Alloys and Compounds* 770, 840–848. doi:10.1016/j.jallcom.2018.08.215.
- Pandey, A.B., Kendig, K.L., Watson, T.J. (Eds.), 2010. *Affordable Metal-Matrix Composites for High Performance Applications II*. Hoboken, NJ: John Wiley & Sons, Inc. doi:10.1002/9781118787120.
- Pank, D.R., Jackson, J.J., 1993. Metal- matrix composite processing technologies for aircraft engine applications. *Journal of Materials Engineering and Performance* 2 (3), 341–346. doi:10.1007/BF02648820.
- Papazian, J.M., 1988. Effects of SiC whiskers and particles on precipitation in aluminum matrix composites. *Metallurgical Transactions A* 19 A (12), 2945–2953. doi:10.1007/BF02647721.
- Patil, V., *et al.*, 2020. Studies on mechanical behavior and morphology of alumina fibers reinforced with aluminium-4.5% copper alloy metal matrix composites. *Materials Today: Proceedings* (in press). doi:10.1016/j.matpr.2020.06.176.
- Piggott, M.R., 1989. The interface in carbon fibre composites. *Carbon* 27 (5), 657–662. doi:10.1016/0008-6223(89)90199-1.
- Poudens, A., Bacroix, B., 1996. Recrystallization textures in Al-SiC metal matrix composites. *Scripta Materialia* 34 (6), 847–855. doi:10.1016/1359-6462(95)00613-3.
- Qu, X.H., *et al.*, 2011. Review of metal matrix composites with high thermal conductivity for thermal management applications. *Progress in Natural Science: Materials International* 21 (3), 189–197. doi:10.1016/S1002-0071(12)60029-X.
- Rado, C., Drevet, B., Eustathopoulos, N., 2000. Role of compound formation in reactive wetting: The Cu/SiC system. *Acta Materialia* 48 (18–19), 4483–4491. doi:10.1016/S1359-6454(00)00235-4.
- Raghukandan, K., *et al.*, 2004. Microstructural study on underwater shock consolidated Al/SiCp composites. *Materials Science Forum* 465–466, 201–206. doi:10.4028/www.scientific.net/MSF.465-466.201.
- Rajkovic, V., *et al.*, 2014. Processing, characterization and properties of copper-based composites strengthened by low amount of alumina particles. *Powder Technology* 268, 392–400. doi:10.1016/j.powtec.2014.08.051.
- Ravi Chandran, K.S., Panda, K.B., Sahay, S.S., 2004. TiB_w-reinforced Ti composites: Processing, properties, application prospects, and research needs. *JOM* 56 (5), 42–48. doi:10.1007/s11837-004-0127-1.
- Rekha, M.Y., Srivastava, C., 2019. Microstructural evolution and corrosion behavior of ZnNi-graphene oxide composite coatings. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science* 50 (12), 5896–5913. doi:10.1007/s11661-019-05474-9.
- Ren, S., *et al.*, 2008. Effect of controlled interfacial reaction on the microstructure and properties of the SiCp/Al composites prepared by pressureless infiltration. *Journal of Alloys and Compounds* 455 (1–2), 424–431. doi:10.1016/j.jallcom.2007.01.127.
- Rong, T., *et al.*, 2016. Effects of tailored gradient interface on wear properties of WC/Inconel 718 composites using selective laser melting. *Surface and Coatings Technology* 307, 418–427. doi:10.1016/j.surfcoat.2016.09.011.
- Russell, A.M., *et al.*, 1999. A high-strength, high-conductivity Al-Ti deformation processed metal metal matrix composite. *Composites Part A: Applied Science and Manufacturing* 30 (3), 239–247. doi:10.1016/S1359-835X(98)00163-8.
- Samanta, A., Wang, Q., Ding, H., 2018. A novel selective laser melting process for glass fiber-reinforced metal matrix composites. *Manufacturing Letters* 18, 27–30. doi:10.1016/j.mfglet.2018.09.006.
- Saravanan, R.A., Surappa, M.K., 2000. Fabrication and characterisation of pure magnesium-30 vol% SiCP particle composite. *Materials Science and Engineering A* 276 (1–2), 108–116. doi:10.1016/S0921-5093(99)00498-0.
- Sekhar, J.A., Trivedi, R., 1991. Solidification microstructure evolution in the presence of inert particles. *Materials Science and Engineering A* 147 (1), 9–21. doi:10.1016/0921-5093(91)90800-3.
- Semenova, I.P., Valiev, R.Z., Langdon, T.G., 2018. High-pressure torsion and equal-channel angular pressing. In: Garbacz, H., Semenova, I.P., Zhrebtsov, S., Motyka, M. (Eds.), *Nanocrystalline Titanium*. Elsevier, pp. 3–19. doi:10.1016/B978-0-12-814599-9.00001-8.
- Shabadi, R., *et al.*, 2015. Thermal conductivity in yttria dispersed copper. *Materials and Design* 65, 869–877. doi:10.1016/j.matdes.2014.09.083.
- Shahani, R.A., Clyne, T.W., 1991. Recrystallization in fibrous and particulate metal matrix composites. *Materials Science and Engineering A* 135 (C), 281–285. doi:10.1016/0921-5093(91)90576-9.

- Shao, W.Z., *et al.*, 2004. A study on graphitization of diamond in copper-diamond composite materials. *Materials Letters* 58 (1–2), 146–149. doi:10.1016/S0167-577X(03)00433-6.
- Shin, S., *et al.*, 2019. Microstructural evolution and strengthening mechanism of SiC/Al composites fabricated by a liquid-pressing process and heat treatment. *Materials* 12 (20), doi:10.3390/ma12203374.
- Shirvanimoghaddam, K., *et al.*, 2017. Carbon fiber reinforced metal matrix composites: Fabrication processes and properties. *Composites Part A: Applied Science and Manufacturing*. 70–96. doi:10.1016/j.compositesa.2016.10.032.
- Shuvho, M.B.A., *et al.*, 2020. Surface characterization and mechanical behavior of aluminum based metal matrix composite reinforced with nano Al_2O_3 , SiC, TiO_2 particles. *Chemical Data Collections* 28. 100442. doi:10.1016/j.cdc.2020.100442.
- Song, M., Huang, B., 2008. Effects of particle size on the fracture toughness of SiCp/Al alloy metal matrix composites. *Materials Science and Engineering A* 488 (1–2), 601–607. doi:10.1016/j.msea.2008.03.022.
- Sree Manu, K.M., *et al.*, 2016. Liquid metal infiltration processing of metallic composites: A critical review. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science* 47 (5), 2799–2819. doi:10.1007/s11663-016-0751-5.
- Srivastava, N., Chaudhari, G.P., 2018. Microstructural evolution and mechanical behavior of ultrasonically synthesized Al6061-nano alumina composites. *Materials Science and Engineering A* 724, 199–207. doi:10.1016/j.msea.2018.03.092.
- Staab, G.H., 1999. Introduction to composite materials. In: *Laminar Composites*. Butterworth-Heinemann, pp. 1–16. doi:10.1016/B978-075067124-8/50001-1.
- Suárez-Martínez, R., *et al.*, 2020. Ti-TiH₂ matrix composites reinforced with TiN by high vacuum sintering (HVS) for biomedical applications. *Materials Letters* 277. 128382doi:10.1016/j.matlet.2020.128382.
- Surappa, M.K., 1997. Microstructure evolution during solidification of DRMMCs (discontinuously reinforced metal matrix composites): State of art. *Journal of Materials Processing Technology* 63 (1–3), 325–333. doi:10.1016/S0924-0136(96)02643-X.
- Suresh, S., Christman, T., Sugimura, Y., 1989. Accelerated aging in cast Al alloy-SiC particulate composites. *Scripta Metallurgica* 23 (9), 1599–1602. doi:10.1016/0036-9748(89)90136-1.
- Suresh, S., Mortensen, A., Needleman, A., 2013. *Fundamentals of Metal-Matrix Composites*. Elsevier. doi:10.1002/9780470905098.ch4.
- Tian, K., *et al.*, 2014. Effects of in situ generated ZrB₂ nano-particles on microstructure and tensile properties of 2024Al matrix composites. *Journal of Alloys and Compounds*. 1–6. doi:10.1016/j.jallcom.2014.01.117.
- Tsuji, N., 2011. Bulk nanostructured metals and alloys produced by accumulative roll-bonding. In: Whang, S.H. (Ed.), *Nanostructured Metals and Alloys: Processing, Microstructure, Mechanical Properties and Applications*. Elsevier, pp. 40–58. doi:10.1533/9780857091123.1.40.
- Uan, J.Y., Chen, L.H., Lui, T.S., 2001. On the extrusion microstructural evolution of Al-AlNi in situ composite. *Acta Materialia* 49 (2), 313–320. doi:10.1016/S1359-6454(00)00309-8.
- Vancheeswaran, R., Meyer, D.G., Wadley, H.N.G., 1997. Optimizing the consolidation of titanium matrix composites. *Acta Materialia* 45 (10), 4001–4018. doi:10.1016/S1359-6454(97)00104-3.
- Vogelsang, M., Arsenaault, R.J., Fisher, R.M., 1986. An in situ HVEM study of dislocation generation at Al/SiC interfaces in metal matrix composites. *Metallurgical Transactions A* 17 (3), 379–389. doi:10.1007/BF02643944.
- Vorozhtsov, S., *et al.*, 2017. Structural and mechanical properties of aluminium-based composites processed by explosive compaction. *Powder Technology* 313, 251–259. doi:10.1016/j.powtec.2017.03.027.
- Wang, M., *et al.*, 2020. Achieving high ductility in layered carbon nanotube/copper composite prepared by composite electrodeposition. In: Haenen, K. (Ed.), *Diamond and Related Materials* 108. Elsevier.107992. doi:10.1016/j.diamond.2020.107992.
- Wang, S., *et al.*, 2019. Facile electrodeposition of three-dimensional flower-like structure of nickel matrix composite electrodes for hydrogen evolution reaction. *Applied Surface Science* 498. 143768. doi:10.1016/j.apsusc.2019.143768.
- Wang, X., Jha, A., Brydson, R., 2004. In situ fabrication of Al₃Ti particle reinforced aluminium alloy metal-matrix composites. *Materials Science and Engineering A* 364 (1–2), 339–345. doi:10.1016/j.msea.2003.08.049.
- Wang, Y., *et al.*, 2014a. In situ formed core-shell structured particle reinforced aluminum matrix composites. *Materials and Design* 56, 405–408. doi:10.1016/j.matdes.2013.11.030.
- Wang, Z., *et al.*, 2014b. Fabrication and mechanical properties of Al-based metal matrix composites reinforced with Mg₆₅Cu₂₀Zn₅Y₁₀ metallic glass particles. *Materials Science and Engineering A* 600, 53–58. doi:10.1016/j.msea.2014.02.003.
- Weber, L., Tavangar, R., 2007. On the influence of active element content on the thermal conductivity and thermal expansion of Cu-X (X = Cr, B) diamond composites. *Scripta Materialia* 57 (11), 988–991. doi:10.1016/j.scriptamat.2007.08.007.
- Wei, S.L., *et al.*, 2018. Interactive effects of cyclic oxidation and structural evolution for Ti-6Al-4V/(TiC + TiB) alloy composites at elevated temperatures. *Journal of Alloys and Compounds* 752, 164–178. doi:10.1016/j.jallcom.2018.04.118.
- Werwer, M., Cornec, A., Schwalbe, K.H., 1998. Local strain fields and global plastic response of continuous fiber reinforced metal-matrix composites under transverse loading. *Computational Materials Science* 12 (2), 124–136. doi:10.1016/S0927-0256(98)00037-8.
- White, J., Willis, T.C., 1989. The production of metal matrix composites by spray deposition. *Materials and Design* 10 (3), 121–127. doi:10.1016/S0261-3069(89)80027-5.
- Wu, K., *et al.*, 2010. Microstructure and mechanical properties of the Mg/Al laminated composite fabricated by accumulative roll bonding (ARB). *Materials Science and Engineering A* 527 (13–14), 3073–3078. doi:10.1016/j.msea.2010.02.001.
- Wu, Q., Xu, W., Zhang, L., 2019. Microstructure-based modelling of fracture of particulate reinforced metal matrix composites. *Composites Part B: Engineering* 163, 384–392. doi:10.1016/j.compositesb.2018.12.099.
- Xiang, Y., *et al.*, 2019. Achieving ultra-high strengthening and toughening efficiency in carbon nanotubes/magnesium composites via constructing micro-nano layered structure. *Composites Part A: Applied Science and Manufacturing* 119, 225–234. doi:10.1016/j.compositesa.2019.02.006.
- Xiao, Y., *et al.*, 2019. Microstructural characteristics and evolution of in situ xTiB₂/Al-20%Si alloy. *Materials Research Express* 6 (12), doi:10.1088/2053-1591/ab69c0.
- Xiong, D.B., *et al.*, 2015. Graphene-and-copper artificial nacre fabricated by a preform impregnation process: Bioinspired strategy for strengthening-toughening of metal matrix composite. *ACS Nano* 9 (7), 6934–6943. doi:10.1021/acsnano.5b01067.
- Yan, H., *et al.*, 2020. Fabrication and tribological behaviors of Ti₃SiC₂/Ti₅Si₃/TiC/Ni-based composite coatings by laser cladding for self-lubricating applications. *Optics and Laser Technology* 126. 106077. doi:10.1016/j.optlastec.2020.106077.
- Yang, B., *et al.*, 2003. TiC particulate-reinforced Al-20Si-5Fe composite fabricated by melt in situ reaction spray forming. *Journal of Materials Processing Technology* 137 (1–3 SPEC), 187–190. doi:10.1016/S0924-0136(02)01094-4.
- Yang, X., *et al.*, 2018. Refinement of LPSO structure in Mg-Ni-Y alloys by ultrasonic treatment. *Ultrasonics Sonochemistry* 40, 472–479. doi:10.1016/j.ultrsonch.2017.07.042.
- Yang, Y., Lan, J., Li, X., 2004. Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Materials Science and Engineering A* 380 (1), 378–383. doi:10.1016/j.msea.2004.03.073.
- Yao, X., *et al.*, 2015. Microstructures and tensile mechanical properties of an ultrafine grained AA6063–5 vol%SiC metal matrix nanocomposite synthesized by powder metallurgy. *Materials Science and Engineering A* 648, 225–234. doi:10.1016/j.msea.2015.09.059.
- Yuan, C.H., *et al.*, 2020. Processing map and hot deformation behavior of Ta-particle reinforced TiAl composite. *Transactions of Nonferrous Metals Society of China* 30 (3), 657–667. doi:10.1016/S1003-6326(20)65240-2.
- Zhang, J., *et al.*, 2020a. Microstructural evolution of hybrid aluminum matrix composites reinforced with SiC nanoparticles and graphene/graphite prepared by powder metallurgy. *Progress in Natural Science: Materials International* January, 1–8. doi:10.1016/j.pnsc.2020.01.024.

- Zhang, J.Y., *et al.*, 2020b. Simultaneously strengthening and toughening a core-shell structured particulate reinforced aluminum alloy-based composite by solid solution treatment. *Journal of Alloys and Compounds* 842, 155765. doi:10.1016/j.jallcom.2020.155765.
- Zhang, L., *et al.*, 2020c. Construction of 3D interconnected diamond networks in Al-matrix composite for high-efficiency thermal management. *Chemical Engineering Journal* 380, 122551. doi:10.1016/j.cej.2019.122551.
- Zhang, X.P., Castagne, S., Yang, T.H., Gu, C.F., Wang, J.T., 2011a. Entrance analysis of 7075 Al/Mg-Gd-Y-Zr/7075 Al laminated composite prepared by hot rolling and its mechanical properties. *Materials and Design* 32 (3), 1152–1158. doi:10.1016/j.matdes.2010.10.030.
- Zhang, X.P., Yang, T.H., Castagne, S., Wang, J.T., 2011b. Microstructure; Bonding strength and thickness ratio of Al/Mg/Al alloy laminated composites prepared by hot rolling. *Materials Science and Engineering A* 528 (4–5), 1954–1960. doi:10.1016/j.msea.2010.10.105.
- Zhao, S., *et al.*, 2018. Densification behavior and mechanical properties of nanocrystalline TiC reinforced 316L stainless steel composite parts fabricated by selective laser melting. *Optics and Laser Technology* 103, 239–250. doi:10.1016/j.optlastec.2018.01.005.
- Zhilyaev, A.P., Langdon, T.G., 2008. Using high-pressure torsion for metal processing: Fundamentals and applications. *Progress in Materials Science*, 893–979. doi:10.1016/j.pmatsci.2008.03.002.
- Zhong, T., *et al.*, 2014. Hot deformation mechanisms, microstructure and texture evolution in extruded AZ31–nano-alumina composite. *Materials Science and Engineering A* 589, 41–49. doi:10.1016/j.msea.2013.09.062.
- Zhou, M.Y., *et al.*, 2019. Achieving ultra-high strength and good ductility in AZ61 alloy composites containing hybrid micron SiC and carbon nanotubes reinforcements. *Materials Science and Engineering A* 768, 138447. doi:10.1016/j.msea.2019.138447.
- Zhou, M.Y., *et al.*, 2020. Progress in research on hybrid metal matrix composites. *Journal of Alloys and Compounds* 838, 155274. doi:10.1016/j.jallcom.2020.155274.
- Zhu, B., Liang, W., Li, X., 2011. Interfacial microstructure, bonding strength and fracture of magnesium-aluminum laminated composite plates fabricated by direct hot pressing. *Materials Science and Engineering A* 528 (21), 6584–6588. doi:10.1016/j.msea.2011.05.015.
- Zuo, T., *et al.*, 2020. Enhanced electrical conductivity and hardness of Copper/carbon nanotubes composite by tuning the interface structure. *Materials Letters*, 128564. doi:10.1016/j.matlet.2020.128564.

Tensile Characteristics of Metal Matrix Composites

Milli S Kujur, Ved P Dubey, and Ashis Mallick, Indian Institute of Technology (Indian School of Mines) Dhanbad, Dhanbad, India
Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Light weighting has become a necessity for applications in automotive and aerospace sectors and to push prospective buyers for a client decision. With skyrocketing oil costs and policies to embolden cut in greenhouse gas emissions is heavily influencing researchers, scientists, manufacturers and industries to stress on lightweight materials (Gupta and Ling, 2011). Also, adapting lightweight materials to build components such as engines, seats and frames for automobile and airplane would help to reduce CO₂ emissions hence increasing fuel efficiency and control pollution. Magnesium (Mg) has a density of 1.74 g/cc, which is 33% lighter than aluminum, 61% lighter than titanium and 77% lighter than stainless steel, thus making it extremely lightweight structural metal easily available on earth's crust (Kumar *et al.*, 2018b). Additionally, with properties such as high specific strength, excellent castability, resistance to electromagnetic radiation, machinability, mechanical and thermal properties make it attractive to be used for engineering applications (Kaiser and Kainer, 2003). However, plastic deformation of Mg is strongly affected by its HCP crystal structure and it exhibits limited ductility (5%–8%) at room temperature (Gehrmann *et al.*, 2005). Low elastic modulus and the high price of magnesium are some of its additional limitations that hinder its marketing. The elastic modulus of magnesium (40–45 GPa) is almost like that of cortical bone (15–30 GPa).

Further, Mg has excellent biocompatibility and would not pose any toxicity to human cells (Parande *et al.*, 2020). Mg-based materials are beneficial for biomedical applications and have advantages over many biodegradable materials such as polymers, ceramics and bioactive glasses, particularly in load-bearing applications requiring higher strengths (Dyadyura and Sukhodub, 2017). Metallic implants like Ti-6Al-4V (113.8 GPa), 316L stainless steel (193 GPa) and Co-Cr alloy (220–240 GPa) have higher elastic modulus and if implanted inside the body would offer stress-shielding effects leading to additional surgery and patient morbidity (Kujur *et al.*, 2017). Magnesium as an implant would not offer any stress-shielding effects, and being biodegradable would dissolve inside the human body. But the poor corrosion resistance of magnesium impedes its clinical application. These limitations of magnesium can be circumvented with proper selection of (1) alloying elements; and (2) addition of inexpensive nanoparticulate (Kujur *et al.*, 2018; Wakeel *et al.*, 2018; Kujur *et al.*, 2019). Micron-size reinforcements, due to their larger size if embedded in the matrix, have a higher probability of containing fracture initiating defects, making particle fracture more prevalent. Further, micron-size reinforcements are generally seen to lead substantial reduction in the ductility of the magnesium matrix due to particle cracking and void formation at particle-matrix interface leading to accelerated failure. Addition of alloying elements is already known to improve the properties for the base matrix (Wakeel *et al.*, 2018). The inclusion of nanoparticulates in the base matrix would improve the properties of overall mechanical strength and ductility through dispersion strengthening without altering its density (Wakeel *et al.*, 2018). The composites with a small volume fraction of nano-size reinforcements have shown the results that are comparable or even sometimes superior to the composites reinforced with micron-size reinforcement at the same or higher volume fraction (Tjong, 2007; Casati and Vedani, 2014). Nanocomposites are lightweight materials which generally incorporate lower volume percentage of nanoparticles in their base matrix (Kujur *et al.*, 2018). Previous papers show the incorporation of oxides, nitrides, carbides, borides, hollow and amorphous nano-reinforcements to Mg and Mg-alloy (Gupta and Wong, 2015). The significant improvement in ductility and corrosion resistance can be seen in the published research works. Thus, to attempt the development of magnesium based nanocomposites is very much promising to serve in more extensive areas of structural and biomedical applications (Wong and Gupta, 2016).

Critically optimized techniques are opted to synthesize Mg-based nanocomposites. The typical processing methods used to synthesis magnesium metal nanocomposites are: (1) liquid state process: stir casting, ultrasonic assisted casting, infiltration process, disintegrated melt deposition (DMD), high pressure die casting; (2) solid state process: mechanical alloying, microwave sintering, bi-directional hybrid microwave sintering; (3) semi-solid state process: thixoprocessing; (4) friction stir processing (5) in-situ synthesis (Ceschini *et al.*, 2017a). Of attention is the liquid and semi-solid processing techniques, since they are potentially scalable to industrial level for the high-volume production of near-net-shape components (Ceschini *et al.*, 2017b). However, the general aim is to uniformly disperse the reinforcements and avoid agglomeration and achieve wettability throughout the matrix through a proper production route such that there won't be any detrimental effect on the mechanical properties. Particularly, disintegrated melt deposition (DMD) and powder metallurgy incorporating hybrid microwave sintering technique are two such methods where uniform dispersion of nano-reinforcements in the matrix is achievable. The hybrid microwave sintering is an energy-efficient and an environment-friendly technique. This method eliminates the usage of any inert gas or vacuum system for sintering, thus reducing the processing time significantly (Kumar *et al.*, 2018b). The Disintegrated Melt Deposition (DMD) technique is a modification of spray atomization and deposition technique. The DMD method brings together the cost-effectiveness of conventional casting and the scientific innovativeness and technological potential of the spray process (Parande *et al.*, 2018). Further, the introduction of secondary processing like extrusion after primary processing would give out homogenization of the distribution of reinforcements to improve the properties of composites (Parande *et al.*, 2018). The synthesis of the

nanocomposites of these two methods has shown significant improvement in the tensile strength, hardness, dimensional stability coupled with ductility and good toughness at both room temperature and high temperature (Mallick *et al.*, 2009).

This article focuses on magnesium-based nanocomposites synthesized using two methods: Powder metallurgy (P/M) assisted hybrid microwave sintering and disintegrated melt deposition (DMD) processing techniques. The tensile behavior with the inclusion of various reinforcements is compared as per the published data. This work also highlights the effect of strengthening mechanisms on the mechanical behavior (tensile yield strength (0.2% TYS), ultimate tensile strength (UTS), ductility and work of fracture (WOF)) of the nanocomposites to serve in wider areas of structural and biomedical applications.

Synthesis of Mg-Based Nanocomposites

The presented work shows nanocomposites prepared by (a) powder metallurgy (P/M) followed by hybrid microwave sintering and (b) disintegrated melt deposition (DMD) processing techniques and its significance.

Powder Metallurgy

The powder metallurgy route adapted in this study generally consists of blending, compaction, microwave sintering and hot extrusion. The nanopowders are initially blended in the mixing machine without the usage of balls at a high rotational speed with a limitation until 2 h to disperse the nanoparticles in the base matrix uniformly. The powder is compacted uniaxially to obtain green billets prior to microwave sintering. The secondary process, such as extrusion, is further employed to get rods of 8 mm in diameter.

Disintegrated Melt Deposition (DMD)

The disintegrated melt deposition (DMD) technique implicates the heating of magnesium chips/turnings and nanopowder to a superheated temperature in a graphite crucible. There is a continuous supply of inert gas to the crucible to avoid oxidation of the material. On reaching temperature above 650°C, a mild steel impeller is used to stir the molten slurry for 5 min at 450 rpm. This would ease the uniform dispersion of nanoparticles in the solid medium and maintain the temperature homogeneity. The base of crucible contains an orifice and the molten slurry is discharged through it. The two jet streams of argon gas are sprayed in the direction of melt stream before getting collected in a metallic substrate.

Tensile Properties for Mg-Based Nanocomposites

The experimental data for tensile analysis of Mg-based nanocomposites conducted at room temperature is represented by two different processing techniques. **Tables 1** and **2** denote the tensile yield strength (0.2% TYS), ultimate tensile strength (UTS), ductility and work of fracture (WOF) of the nanocomposites synthesized (a) powder metallurgy method followed by hybrid microwave sintering technique and (b) disintegrated melt deposition technique respectively. It is to be noted that the tensile strengths of the synthesized nanocomposites have been compared to the tensile strength of pure Mg taken from reference (Wong and Gupta, 2017) and (Hassan and Gupta, 2007a) respectively irrespective of their processing techniques to understand the percentage of improvement with nanoreinforcement addition in comparison to the base matrix.

The tensile properties for the Mg-based nanocomposites were determined as per ASTM E8M-01. It is clear from the results that with the addition of nanoparticles (metallic, ceramic and hybrid) in the base matrix, the 0.2% TYS, UTS and ductility (~ mostly) is seen to improve. However, the results also further show the increase or decrease in the tensile strength varying depending on the distribution and agglomeration of the nanoparticles embedded in the Mg matrix. Unlike micron size composites, the significant improvement in tensile strength displayed by the nanocomposites is noteworthy.

Table 1 presents the 0.2% tensile yield strength (TYS), ultimate tensile strength (UTS), ductility and work of fracture (WOF) for magnesium matrix composites embedded with micron-size and nano-size particles along with some of the commercially available alloys synthesized by powder metallurgy technique followed by microwave sintering. As seen from **Table 1**, Tun *et al.* included ZnO in pure Mg by powder metallurgy method incorporating hybrid microwave sintering followed by extrusion (Tun *et al.*, 2012). The tensile strength improved for pure Mg with an increasing amount of 0.5, 1.0 and 1.5 vol% of ZnO. Mg/1.0ZnO displayed the best 0.2% TYS (125 MPa), UTS (231 MPa) and ductility (17%) amongst Mg/0.5ZnO and Mg/1.5ZnO nanocomposites. The 0.2% TYS, UTS and ductility improved by 8%, 38% and 179% respectively in comparison to pure Mg. Similarly, with the increasing amount of 0.35, 0.5 and 1.0 vol% of SiC nanoparticle addition in Mg, the tensile property improved simultaneously (Wong and Gupta, 2006). Mg/1.0SiC displayed the best 0.2% TYS (157 MPa), UTS (203 MPa) and ductility (7.6%) amongst Mg/0.35SiC and Mg/0.5SiC nanocomposites. The 0.2% TYS, UTS and ductility for Mg/1.0SiC improved by 35%, 21% and 25% respectively in comparison to pure Mg. It is clear from **Table 1**, Mg/(0.7Y₂O₃ + 0.6Ni) nanocomposite showed the best improvements in the tensile strength property. The results also include the improvement of ductility and work of fracture in Mg/(0.7Y₂O₃ + 0.6Ni) as compared to pure Mg and other presented compositions (Tun and Gupta, 2009). The 0.2% TYS, UTS, ductility and WOF for Mg/(0.7Y₂O₃ + 0.6Ni) was 232 MPa, 272 MPa, 9.5% and 25.9 J/mm³ respectively. The 0.2% TYS, UTS, ductility and WOF improved

Table 1 Room temperature tensile properties of mg-based nanocomposites synthesized by powder metallurgy incorporating hybrid microwave method

Material	0.2% TYS (MPa)	UTS (MPa)	Ductility (%)	Work of fracture (MJ/m ³)
Pure Mg (Wong and Gupta, 2017)	116 ± 11	168 ± 10	6.1 ± 2.0	11.8 ± 3.4
Mg/0.3Cu (Wong and Gupta, 2017)	188 ± 13 (+62%)	218 ± 11 (+30%)	5.9 ± 1.1 (−3%)	12.8 ± 2.0 (+8%)
Mg/0.6Cu (Wong and Gupta, 2017)	237 ± 24 (+104%)	286 ± 8 (+70%)	5.4 ± 1.2 (−11%)	16.5 ± 3.1 (+40%)
Mg/1.0Cu (Wong and Gupta, 2017)	194 ± 17 (+67%)	221 ± 17 (+32%)	2.9 ± 0.4 (−52%)	6.8 ± 1.0 (−42%)
Mg/0.3Al ₂ O ₃ (Wong and Gupta, 2017)	119 ± 7 (+3%)	175 ± 8 (+4%)	7.5 ± 0.2 (+23%)	–
Mg/0.6Al ₂ O ₃ (Wong and Gupta, 2017)	130 ± 5 (+12%)	180 ± 7 (+7%)	7.4 ± 0.3 (+21%)	–
Mg/1.0Al ₂ O ₃ (Wong and Gupta, 2017)	154 ± 5 (+33%)	213 ± 12 (+27%)	6.3 ± 0.4 (+3%)	–
Mg/0.3ZrO ₂ (Tun et al., 2013)	85 ± 8 (−27%)	139 ± 8 (−17%)	8.1 ± 1.6 (+33%)	–
Mg/0.6ZrO ₂ (Tun et al., 2013)	117 ± 11 (+1%)	182 ± 14 (+8%)	9.4 ± 2.7 (+54%)	–
Mg/1.0ZrO ₂ (Tun et al., 2013)	98 ± 6 (−16%)	158 ± 12 (−6%)	8.6 ± 2.2 (+41%)	–
Mg/(0.3ZrO ₂ + 0.7Cu) (Tun et al., 2013)	196 ± 16 (+69%)	249 ± 8 (+48%)	8.2 ± 1.1 (+34%)	–
Mg/(0.6ZrO ₂ + 0.4Cu) (Tun et al., 2013)	139 ± 22 (+20%)	193 ± 21 (+15%)	11.4 ± 2.9 (+87%)	–
Mg/0.35SiC (Wong and Gupta, 2006)	132 ± 14 (+14%)	194 ± 11 (+15%)	6.3 ± 1.0 (+3%)	–
Mg/0.5SiC (Wong and Gupta, 2006)	144 ± 12 (+24%)	194 ± 10 (+15%)	7.0 ± 2.0 (+15%)	–
Mg/1.0SiC (Wong and Gupta, 2006)	157 ± 22 (+35%)	203 ± 22 (+21%)	7.6 ± 1.5 (+25%)	–
Mg/10 vol% SiC (μm) (Wong and Gupta, 2006)	120 (+3%)	160 (−5%)	2 (−67%)	–
Mg/0.17Y ₂ O ₃ (Tun and Gupta, 2007)	144 ± 2 (+24%)	214 ± 4 (+27%)	8.0 ± 2.8 (+31%)	16.6 ± 4.2 (+41%)
Mg/0.7Y ₂ O ₃ (Tun and Gupta, 2007)	157 ± 10 (+35%)	244 ± 1 (+45%)	9.1 ± 0.6 (+49%)	21.8 ± 3.1 (+85%)
Mg/(0.7 Y ₂ O ₃ + 0.3Ni) (Tun and Gupta, 2009)	221 ± 7 (+91%)	262 ± 6 (+56%)	9.0 ± 0.9 (+48%)	23.7 ± 2.1 (+101%)
Mg/(0.7Y ₂ O ₃ + 0.6Ni) (Tun and Gupta, 2009)	232 ± 8 (+100%)	272 ± 2 (+62%)	9.5 ± 0.9 (+56%)	25.9 ± 2.3 (+119%)
Mg/(0.7 Y ₂ O ₃ + 1.0Ni) (Tun and Gupta, 2009)	228 ± 8 (+97%)	271 ± 6 (+61%)	5.5 ± 0.7 (−10%)	15.4 ± 2.3 (+31%)
Mg/(0.7 Y ₂ O ₃ + 0.3Cu) (Tun et al., 2010)	215 ± 20 (+85%)	270 ± 22 (+61%)	11.1 ± 1.0 (+82%)	29.8 ± 2.7 (+153%)
Mg/(0.7 Y ₂ O ₃ + 0.6Cu) (Tun et al., 2010)	179 ± 7 (+54%)	231 ± 13 (+38%)	11.1 ± 0.7 (+82%)	25.4 ± 0.9 (+115%)
Mg/0.22B ₄ C (Habibi et al., 2013)	110 ± 15 (+5%)	159 ± 14 (−5%)	9.9 ± 0.6 (+62%)	–
Mg/0.66B ₄ C (Habibi et al., 2013)	120 ± 5 (+3%)	164 ± 6 (−3%)	10.0 ± 0.3 (+64%)	–
Mg/1.11B ₄ C (Habibi et al., 2013)	82 ± 11 (−29%)	119 ± 17 (−29%)	5.5 ± 1.2 (−10%)	–
Mg/0.92Al-0.66B ₄ C (Habibi et al., 2013)	130 ± 9 (+12%)	238 ± 15 (+42%)	7.0 ± 0.9 (+15%)	–
Mg/0.25Al (Zhong et al., 2007)	181 ± 14 (+56%)	221 ± 15 (+32%)	4.8 ± 0.4 (−21%)	10.5 ± 1.9 (−11%)
Mg/0.5Al (Zhong et al., 2007)	218 ± 16 (+88%)	271 ± 11 (+61%)	6.2 ± 0.9 (+2%)	15.9 ± 2.1 (+35%)
Mg/0.75Al (Zhong et al., 2007)	202 ± 7 (+74%)	261 ± 10 (+55%)	5.0 ± 1.6 (−18%)	13.1 ± 2.9 (+11%)
Mg/1.0Al (Zhong et al., 2007)	185 ± 9 (+59%)	226 ± 12 (+35%)	3.3 ± 1.0 (−46%)	7.9 ± 1.8 (−33%)
Mg/0.5ZnO (Tun et al., 2012)	119 ± 9 (+3%)	203 ± 17 (+21%)	16 ± 2 (+162%)	–
Mg/1.0ZnO (Tun et al., 2012)	125 ± 4 (+8%)	231 ± 13 (+38%)	17 ± 2 (+179%)	–
Mg/1.5ZnO (Tun et al., 2012)	125 ± 4 (+8%)	229 ± 4 (+36%)	17 ± 2 (+179%)	–
Mg/0.5BN (Seetharaman et al., 2013)	127 ± 6 (+9%)	192 ± 8 (+14%)	7.8 ± 0.9 (+28%)	–
Mg/1.5BN (Seetharaman et al., 2013)	142 ± 4 (+22%)	200 ± 5 (+19%)	8.6 ± 0.5 (+41%)	–
Mg/2.5BN (Seetharaman et al., 2013)	145 ± 3 (+25%)	217 ± 5 (+29%)	7.2 ± 0.8 (+18%)	–
Mg/0.5SiO ₂ (Parande et al., 2017)	85 ± 2 (−27%)	136 ± 1 (−19%)	8.6 ± 2 (+41%)	10.1 ± 0.7 (−14%)
Mg/1.0SiO ₂ (Parande et al., 2017)	94 ± 3 (−19%)	150 ± 2 (−11%)	10.5 ± 0.8 (+72%)	14.3 ± 2.1 (+21%)
Mg/2.0SiO ₂ (Parande et al., 2017)	114 ± 5 (−2%)	171 ± 8 (+2%)	6.3 ± 1.7 (+3%)	9.5 ± 3 (−20%)
Mg/0.33TiO ₂ (Hassan et al., 2018)	127 (+9%)	204 (+21%)	10.6 (+74%)	18.1 (+53%)
Mg/0.66TiO ₂ (Hassan et al., 2018)	114 (−2%)	197 (+17%)	12.7 (+108%)	21.5 (+82%)
Mg/1.0TiO ₂ (Hassan et al., 2018)	114 (−2%)	188 (+12%)	11.8 (+93%)	18.9 (+60%)
Mg/1.98TiO ₂ (Meenashisundaram et al., 2015b)	88 ± 10 (−24%)	132 ± 8 (−21%)	14.5 ± 1 (+138%)	17.5 ± 0 (+48%)
Mg/2.5TiO ₂ (Meenashisundaram et al., 2015a)	91.1 ± 5 (−21%)	134 ± 7 (−20%)	6 ± 1 (−2%)	8.6 ± 0.6 (−27%)
Mg-3Al (Kumar et al., 2018a)	133 (+15%)	227.43 (+35%)	11.28 (+85%)	–
Mg-3Al/0.1GNP (Kumar et al., 2018a)	141 (+22%)	238.44 (+42%)	10.12 (+66%)	–

by 100%, 62%, 56% and 119%, respectively. Additionally, SiC particle in its micron size and nano-size has been added in pure Mg by powder metallurgy technique to understand its tensile nature. The yield strength and tensile strength improved for the micron-based composites, whereas there was significant reduction in ductility in comparison to pure Mg (Wong and Gupta, 2006). Whereas, for the Mg/SiC nanocomposites, the incorporation of nano reinforcements helped in improving the overall tensile properties of nanocomposites without reducing its ductility (Wong and Gupta, 2006).

Table 2 presents the 0.2% tensile yield strength (TYS), ultimate tensile strength (UTS), ductility and work of fracture (WOF) for magnesium matrix composites embedded with micron-size and nano-size particles along with some of the commercially available alloys synthesized by disintegrated melt deposition (DMD) technique. **Fig. 1** (data extracted from Hasan et al. Hassan and Gupta (2007a)) compared the room temperature tensile behavior of pure Mg and Mg/xY₂O₃ nanocomposites. As seen from **Fig. 1**, the tensile yield strength and ultimate tensile strength improved with the addition of 0.22, 0.66 and 1.11 vol% of Y₂O₃ nanoparticles. The

Table 2 Room temperature tensile properties of Mg-based nanocomposites synthesized by disintegrated melt deposition method

Materials	0.2% TYS (MPa)	UTS (MPa)	Ductility (%)	Work of Fracture (MJ/m ³)
Pure Mg (Hassan and Gupta, 2007a)	97 ± 2	173 ± 1	7.4 ± 0.2	11.1 ± 0.3
Mg/0.22Y ₂ O ₃ (Hassan and Gupta, 2007a)	218 ± 2 (+125%)	277 ± 5 (+60%)	12.7 ± 1.3 (+72%)	29.6 ± 3.5 (+167%)
Mg/0.66Y ₂ O ₃ (Hassan and Gupta, 2007a)	312 ± 4 (+222%)	318 ± 2 (+84%)	6.9 ± 1.6 (−7%)	18.2 ± 4.7 (+64%)
Mg/1.11Y ₂ O ₃ (Hassan and Gupta, 2007a)	–	205 ± 3 (+18%)	1.7 ± 0.5 (−77%)	1.9 ± 0.7 (−83%)
Mg/0.5Y ₂ O ₃ (Goh <i>et al.</i> , 2007)	141 ± 7 (+45%)	223 ± 5 (+29%)	8.5 ± 1.6 (+15%)	–
Mg/1.0Y ₂ O ₃ (Goh <i>et al.</i> , 2007)	151 ± 5 (+56%)	222 ± 4 (+28%)	6.8 ± 0.5 (−8%)	–
Mg/2.0Y ₂ O ₃ (Goh <i>et al.</i> , 2007)	162 ± 10 (+67%)	227 ± 11 (+31%)	7.0 ± 0.5 (−5%)	–
Mg/0.22Al ₂ O ₃ (Hassan and Gupta, 2004)	146 ± 5 (+51%)	207 ± 11 (+20%)	8.0 ± 2.3 (+8%)	–
Mg/0.66Al ₂ O ₃ (Hassan and Gupta, 2004)	170 ± 4 (+75%)	229 ± 2 (+32%)	2.4 ± 2.1 (−68%)	–
Mg/1.11Al ₂ O ₃ (Hassan and Gupta, 2004)	175 ± 3 (+80%)	246 ± 3 (+42%)	14.0 ± 2.4 (+89%)	31.7 ± 6.3 (+186%)
Mg/0.7Al ₂ O ₃ (Hassan and Gupta, 2008)	214 ± 4 (+121%)	261 ± 5 (+51%)	12.5 ± 1.8 (+69%)	28.9 ± 4.7 (+160%)
Mg/1.11Al ₂ O ₃ (0.3 µm) (Hassan and Gupta, 2008)	200 ± 1 (+106%)	256 ± 1 (+48%)	8.6 ± 1.1 (+16%)	20.9 ± 2.8 (+88%)
Mg/2.5Al ₂ O ₃ (0.3 µm) (Hassan and Gupta, 2008)	222 ± 2 (+129%)	281 ± 5 (+62%)	4.5 ± 0.5 (−39%)	10.0 ± 1.3 (−10%)
Mg/1.11Al ₂ O ₃ (1.0 µm) (Hassan and Gupta, 2006)	209 ± 1 (+115%)	242 ± 3 (+40%)	3.5 ± 0.3 (−53%)	–
Mg/0.22ZrO ₂ (Hassan and Gupta, 2007b)	186 ± 2 (+92%)	248 ± 4 (+43%)	4.7 ± 0.2 (−36%)	–
Mg/0.66ZrO ₂ (Hassan and Gupta, 2007b)	221 ± 5 (+128%)	271 ± 6 (+57%)	4.8 ± 0.7 (−35%)	–
Mg/1.11ZrO ₂ (Hassan and Gupta, 2007b)	216 ± 4 (+123%)	250 ± 6 (+45%)	3.0 ± 0.2 (−59%)	–
Mg/0.3CNT (Goh <i>et al.</i> , 2006)	128 ± 6 (+32%)	194 ± 9 (+12%)	12.7 ± 1.6 (+72%)	–
Mg/1.3CNT (Goh <i>et al.</i> , 2006)	140 ± 2 (+44%)	210 ± 4 (+21%)	13.5 ± 2.0 (+82%)	–
Mg/1.6CNT (Goh <i>et al.</i> , 2006)	121 ± 5 (+25%)	200 ± 3 (+16%)	12.2 ± 2.7 (+65%)	–
Mg/2.0CNT (Goh <i>et al.</i> , 2006)	122 ± 7 (+26%)	198 ± 8 (+14%)	7.7 ± 1.0 (+4%)	–
Mg/0.16ZnO (Sankaranarayanan <i>et al.</i> , 2014a)	119 ± 11 (+23%)	204 ± 9 (+18%)	15 ± 1.4 (+103%)	–
Mg/0.48ZnO (Sankaranarayanan <i>et al.</i> , 2014a)	131 ± 6 (+35%)	210 ± 8 (+21%)	16.3 ± 1.4 (+120%)	–
Mg/0.8ZnO (Sankaranarayanan <i>et al.</i> , 2014a)	147 ± 9 (+52%)	237 ± 8 (+37%)	11.88 ± 1.7 (+61%)	–
Mg/0.58TiB ₂ (Meenashisundaram <i>et al.</i> , 2014)	93 ± 7 (−4%)	149 ± 9 (−14%)	13 ± 0.5 (+76%)	17 ± 0.4 (+53%)
Mg/0.97TiB ₂ (Meenashisundaram <i>et al.</i> , 2014)	110 ± 3 (+13%)	173 ± 8 (0%)	16 ± 0.5 (+116%)	25 ± 2 (+125%)
Mg/1.98TiB ₂ (Meenashisundaram <i>et al.</i> , 2014)	140 ± 9 (+44%)	186 ± 1 (+8%)	14 ± 1 (+89%)	24 ± 2 (+116%)
Mg/0.5NiTi (Parande <i>et al.</i> , 2018)	106 ± 12 (+9%)	167 ± 14 (−3%)	9 ± 0.8 (+22%)	24 ± 1.8 (+116%)
Mg/1NiTi (Parande <i>et al.</i> , 2018)	123 ± 2 (+27%)	176 ± 9 (+2%)	9 ± 4.2 (+22%)	14 ± 1.6 (+26%)
Mg/1.5NiTi (Parande <i>et al.</i> , 2018)	163 ± 9 (+68%)	187 ± 8 (+8%)	9 ± 0.4 (+22%)	14 ± 2.1 (+26%)
Mg/3NiTi (Parande <i>et al.</i> , 2018)	193 ± 17 (+99%)	217 ± 16 (+25%)	11 ± 0.2 (+49%)	23 ± 2.4 (+107%)
Mg/0.58TiO ₂ (Meenashisundaram <i>et al.</i> , 2015a)	80 ± 2 (−18%)	128 ± 3 (−26%)	10 ± 0.5 (+35%)	11.5 ± 3 (+4%)
Mg/0.97TiO ₂ (Meenashisundaram <i>et al.</i> , 2015a)	97 ± 3 (0%)	154 ± 7 (−11%)	10.8 ± 1 (+46%)	15 ± 1.5 (+35%)
Mg/1.98TiO ₂ (Meenashisundaram <i>et al.</i> , 2015a)	102 ± 3 (+5%)	165.5 ± 3 (−4%)	11.5 ± 1 (+55%)	18 ± 0.7 (+62%)
Mg/2.5TiO ₂ (Meenashisundaram <i>et al.</i> , 2015a)	124 ± 8.8 (+28%)	170 ± 6 (−2%)	10 ± 1 (+35%)	16 ± 2 (+44%)
Mg/0.10GNPs (Xiang <i>et al.</i> , 2017)	105 ± 1 (+8%)	176 ± 2 (+2%)	10.3 ± 0.6 (+39%)	17 ± 2 (+53%)
Mg/0.25GNPs (Xiang <i>et al.</i> , 2017)	122 ± 2 (+26%)	202 ± 3 (+17%)	14.5 ± 1.2 (+96%)	27 ± 3 (+143%)
Mg/0.35B ₄ C (Sankaranarayanan <i>et al.</i> , 2014b)	127 ± 6 (+31%)	202 ± 6 (+17%)	11.8 ± 1.6 (+59%)	11.8 ± 1.6 (+6%)
Mg/1.04B ₄ C (Sankaranarayanan <i>et al.</i> , 2014b)	137 ± 5 (+41%)	215 ± 8 (+24%)	17.4 ± 2.0 (+135%)	17.4 ± 2.0 (+57%)
Mg/1.74B ₄ C (Sankaranarayanan <i>et al.</i> , 2014b)	160 ± 2 (+65%)	240 ± 5 (+39%)	12.4 ± 1.7 (+68%)	12.4 ± 1.7 (+12%)
Mg/0.58TiC (Meenashisundaram and Gupta, 2015)	94 ± 3 (−3%)	156 ± 3.5 (−10%)	18 ± 1.5 (+143%)	26 ± 1.5 (+134%)
Mg/0.97TiC (Meenashisundaram and Gupta, 2015)	87 ± 2 (−10%)	149 ± 5 (−14%)	22 ± 0.5 (+197%)	30 ± 2 (+170%)
Mg/1.98TiC (Meenashisundaram and Gupta, 2015)	125 ± 5 (+29%)	190 ± 14 (+10%)	20 ± 1 (+170%)	35.5 ± 3 (+220%)

(Continued)

Table 2 Continued

Materials	0.2% TYS (MPa)	UTS (MPa)	Ductility (%)	Work of Fracture (MJ/m ³)
Mg/0.58Ti (Meenashisundaram and Gupta, 2014)	134 ± 7 (+38%)	190 ± 7 (+10%)	6.3 ± 0.6 (−15%)	11.9 ± 1.5 (+7%)
Mg/0.97Ti (Meenashisundaram and Gupta, 2014)	135 ± 3 (+39%)	197 ± 8 (+14%)	8.3 ± 0.6 (+12%)	16 ± 1 (+44%)
Mg/1.98Ti (Meenashisundaram and Gupta, 2014)	162 ± 5 (+67%)	231 ± 12 (+34%)	7.7 ± 0.1 (+4%)	17.4 ± 0.7 (+57%)
Mg/5.6Ti (19 ± 10 μm) (Hassan and Gupta, 2002a)	163 ± 12 (+68%)	248 ± 9 (+43%)	11.1 ± 1.4 (+50%)	25.7 ± 2.9 (+132%)
Mg/9.6Ti (19 ± 10 μm) (Hassan and Gupta, 2002a)	154 ± 10 (+59%)	239 ± 5 (+38%)	9.5 ± 0.3 (+28%)	20.7 ± 1.4 (+86%)
Mg/0.3BN (Sankaranarayanan <i>et al.</i> , 2015)	133 ± 4 (+37%)	193 ± 7 (+12%)	8.6 ± 0.8 (+16%)	16.5 ± 1.5 (+49%)
Mg/0.6BN (Sankaranarayanan <i>et al.</i> , 2015)	154 ± 2 (+59%)	223 ± 2 (+29%)	15.3 ± 0.6 (+107%)	32.5 ± 1.3 (+193%)
Mg/1.2BN (Sankaranarayanan <i>et al.</i> , 2015)	178 ± 5 (+84%)	255 ± 3 (+47%)	12.6 ± 1.3 (+70%)	32.8 ± 1.4 (+195%)
Mg/0.58TiN (Meenashisundaram <i>et al.</i> , 2016)	91 ± 5 (−6%)	151 ± 4 (−13%)	15 ± 1 (+103%)	20 ± 1 (+80%)
Mg/0.97TiN (Meenashisundaram <i>et al.</i> , 2016)	112 ± 2 (+15%)	173 ± 1 (0%)	15 ± 2 (+103%)	24 ± 2.5 (+116%)
Mg/1.98TiN (Meenashisundaram <i>et al.</i> , 2016)	130 ± 7 (+34%)	190 ± 11 (+10%)	14.5 ± 1 (+96%)	26 ± 4 (+134%)
Mg/2.5TiN (Meenashisundaram <i>et al.</i> , 2016)	135 ± 8 (+39%)	196 ± 14 (+13%)	10.6 ± 1.2 (+43%)	19.8 ± 1 (+78%)
Mg/0.5Zr (Meenashisundaram <i>et al.</i> , 2017)	143.7 ± 10.6 (+48%)	198.3 ± 12.5 (+15%)	10.31 ± 2.2 (+39%)	19.5 ± 3.6 (+76%)
Mg/0.5Zr/1La (Meenashisundaram <i>et al.</i> , 2017)	197 ± 13 (+103%)	210 ± 15 (+21%)	9.4 ± 2.5 (+27%)	19.6 ± 5.5 (+77%)
Mg/0.5Zr/2.5La (Meenashisundaram <i>et al.</i> , 2017)	273 ± 7 (+181%)	250 ± 12 (+45%)	3 ± 1 (−59%)	8.2 ± 0.2 (−26%)
Mg/0.5Zr/4La (Meenashisundaram <i>et al.</i> , 2017)	283 ± 28 (+192%)	296.4 ± 25 (+71%)	3.46 ± 0.4 (−53%)	9.7 ± 2.3 (−13%)
Mg/Ti (μm) (Seetharaman <i>et al.</i> , 2012)	158 ± 6 (+63%)	226 ± 6 (+31%)	6.2 ± 0.7 (−16%)	—
Mg/Cu (Seetharaman <i>et al.</i> , 2012)	182 ± 4 (+88%)	220 ± 4 (+27%)	8.0 ± 1.5 (+8%)	—
Mg/Ti (μm)/Cu (Seetharaman <i>et al.</i> , 2012)	196 ± 9 (+102%)	227 ± 4 (+31%)	8.9 ± 0.9 (+20%)	—
Mg/17.95Cu (8–11 μm) (Hassan and Gupta, 2002c)	355 ± 11 (+266%)	386 ± 3 (+123%)	1.5 ± 0.3 (−80%)	—
Mg/5Nb (μm) (Jayalakshmi <i>et al.</i> , 2012)	129 ± 5 (+33%)	186 ± 5 (+8%)	13.0 ± 11 (+76%)	—
Mg/5Nb (μm)/0.25SiC (Jayalakshmi <i>et al.</i> , 2012)	116 ± 7 (+20%)	164 ± 6 (−5%)	2.2 ± 0.3 (−70%)	—
Mg/5Nb (μm)/0.50SiC (Jayalakshmi <i>et al.</i> , 2012)	116 ± 17 (+20%)	176 ± 15 (+2%)	4.3 ± 0.1 (−42%)	—
Mg/5Nb (μm)/1.0SiC (Jayalakshmi <i>et al.</i> , 2012)	182 ± 10 (+88%)	240 ± 6 (+39%)	2.1 ± 0.2 (−72%)	—
Mg/5Nb (μm)/2.0SiC (Jayalakshmi <i>et al.</i> , 2012)	156 ± 8 (+61%)	208 ± 4 (+20%)	5.1 ± 0.6 (−31%)	—
Mg/10.3 SiC (25 μm) (Gupta <i>et al.</i> , 2000)	127 ± 7.2 (+32%)	195 ± 6.7 (+13%)	6.0 ± 2.3 (−19%)	8.9 ± 2.8 (−20%)
Mg/ 16.0 SiC (25 μm) (Gupta <i>et al.</i> , 2000)	120 ± 4.8 (+24%)	181 ± 5.9 (+5%)	4.7 ± 1.3 (−36%)	8.8 ± 2.0 (−21%)
Mg/21.3 SiC (25 μm) (Gupta <i>et al.</i> , 2000)	128 ± 1.9 (+32%)	176 ± 3.5 (+2%)	1.4 ± 0.1 (−81%)	3.3 ± 0.8 (−70%)
Mg/7.3Ni (29 ± 19 μm) (Hassan and Gupta, 2002b)	337 ± 15 (+247%)	370 ± 14 (+114%)	4.8 ± 1.4 (−35%)	—
Mg/14.0Ni (29 ± 19 μm) (Hassan and Gupta, 2002b)	420 ± 27 (+333%)	463 ± 4 (+168%)	1.4 ± 0.1 (−81%)	—
Mg/24.9Ni (29 ± 19 μm) (Hassan and Gupta, 2002b)	—	313 ± 29 (+81%)	0.7 ± 0.1 (−91%)	—
AZ31B (Nguyen and Gupta, 2008)	201 ± 7 (+107%)	270 ± 6 (+56%)	5.6 ± 1.4 (−24%)	15 ± 3 (+35%)
AZ31B/0.66Al ₂ O ₃ (Nguyen and Gupta, 2008)	149 ± 7 (+54%)	215 ± 15 (+25%)	14.6 ± 1.1 (+97%)	31 ± 4 (+179%)
AZ31B/1.11Al ₂ O ₃ (Nguyen and Gupta, 2008)	148 ± 11 (+53%)	214 ± 16 (+24%)	25.5 ± 2.2 (+245%)	52 ± 2 (+368%)
AZ31B/1.50Al ₂ O ₃ (Nguyen and Gupta, 2008)	144 ± 9 (+48%)	214 ± 16 (+24%)	29.5 ± 1.9 (+299%)	60 ± 3 (+441%)
AZ91A (Ho <i>et al.</i> , 2004)	263 ± 12 (+171%)	358 ± 5 (+107%)	7 ± 4 (−5%)	—
AZ91A/3.59Cu(8–11 μm) (Ho <i>et al.</i> , 2004)	299 ± 5 (+208%)	382 ± 6 (+121%)	6 ± 1 (−19%)	—
ZK60A (Paramsothy <i>et al.</i> , 2011)	163 ± 3 (+68%)	268 ± 3 (+55%)	6.6 ± 0.6 (−11%)	16 ± 2 (+44%)
ZK60A/1.0CNT (Paramsothy <i>et al.</i> , 2011)	180 ± 6 (+86%)	295 ± 8 (+71%)	15.0 ± 0.7 (+103%)	41 ± 1 (+269%)
AZ31 (Alam <i>et al.</i> , 2011)	180 ± 3 (+86%)	273 ± 6 (+58%)	10.6 ± 1.3 (+43%)	27.9 ± 3.9 (+151%)
AZ41 (Alam <i>et al.</i> , 2011)	218 ± 5 (+125%)	287 ± 6 (+66%)	8.2 ± 0.3 (+11%)	23.0 ± 1.4 (+107%)
AZ51 (Alam <i>et al.</i> , 2011)	222 ± 4 (+129%)	302 ± 4 (+75%)	8.7 ± 0.4 (+18%)	27.3 ± 1.2 (+146%)
AZ41/1.50Al ₂ O ₃ (Alam <i>et al.</i> , 2011)	200 ± 2 (+106%)	302 ± 3 (+75%)	12.3 ± 1.2 (+66%)	36.0 ± 3.5 (+224%)

AZ51/1.50Al ₂ O ₃ (Alam <i>et al.</i> , 2011)	211 ± 4 (+ 118%)	311 ± 3 (+ 80%)	13.4 ± 1.2 (+ 81%)	40.7 ± 3.1 (+ 267%)
AZ63 (Meenashisundaram and Gupta, 2014) ^A	75 (– 23%)	180 (+ 4%)	4 (– 46%)	–
AZ81 (Meenashisundaram and Gupta, 2014) ^A	80 (– 18%)	140 (– 19%)	3 (– 59%)	–
AZ91 (Meenashisundaram and Gupta, 2014) ^A	95 (– 2%)	135 (– 22%)	2 (– 73%)	–
AZ31 (Meenashisundaram and Gupta, 2014) ^B	130 (+ 34%)	230 (+ 33%)	4 (– 46%)	–
AZ61 (Meenashisundaram and Gupta, 2014) ^B	180 (+ 86%)	260 (+ 50%)	7 (– 5%)	–
ZK61 (Meenashisundaram and Gupta, 2014) ^B	210 (+ 116%)	285 (+ 65%)	6 (– 19%)	–

*Note: (μm) indicates the size of the particles is in macrons; A indicates composition prepared by sand cast; B indicates wrought magnesium alloys followed by extrusion; (+) indicates the increment and (–) indicates the decrement.

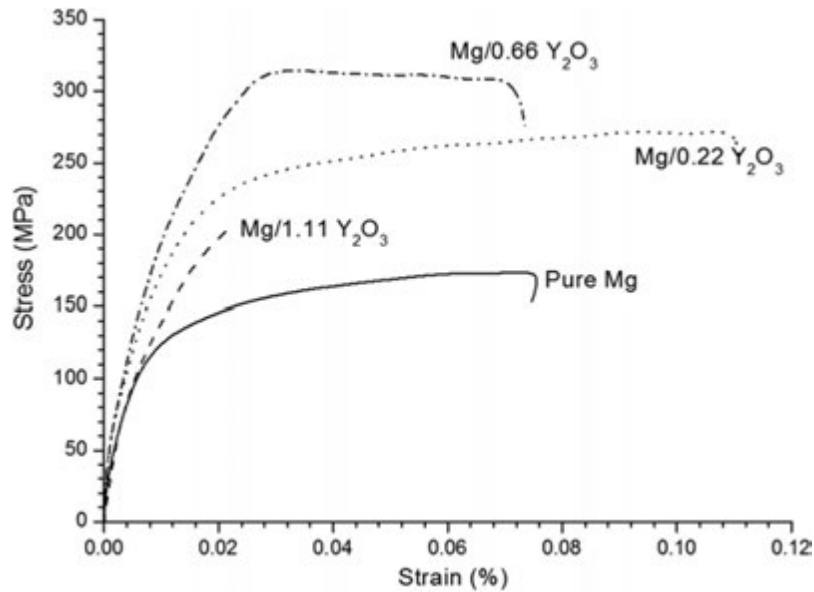


Fig. 1 Representative tensile stress-strain curves of magnesium and its nanocomposites. Data extracted from Hassan, S., Gupta, M., 2007a. Development of nano-Y₂O₃ containing magnesium nanocomposites using solidification processing. *Journal of Alloys and Compounds* 429 (1–2), 176–183.

maximum strength can be seen in the composite when 0.66 vol% Y₂O₃ was used in the Mg matrix. However, a good combination of ductility and strength is observed in Mg/0.22Y₂O₃ nanocomposite. In another study, Goh *et al.* (2006) incorporated 0.3, 1.3, 1.6, 2.0 wt % carbon nanotubes (CNTs) in Mg matrix by DMD technique which resulted in an improvement of 0.2% TYS, UTS, ductility. The 0.2% TYS (140 MPa), UTS (210 MPa) and ductility (13.5%) for Mg/1.3 wt%CNT improved by 44%, 21% and 82% respectively in comparison to pure Mg. The significant improvement in ductility for Mg/1.3 wt%CNT was due to the high activity of basal slip and the initiation of prismatic slip. The ductility was seen to be low for Mg/1.6CNT and Mg/2.0CNT in comparison to Mg/1.3CNT nanocomposite. The possible reason for the reduction of ductility may be due to the agglomeration and cluster formation of CNT nanoparticles in the Mg matrix. From Table 2, it is clear that Mg/0.66Y₂O₃ nanocomposite showed the best improvement in tensile strength property having 0.2% TYS (312 MPa) and UTS (318 MPa) with 222% and 84% increment respectively (Hassan and Gupta, 2007a). Mg/0.97TiC nanocomposite showed best improvement in ductility (22%) with 197% increment and Mg/1.98TiC nanocomposite showed best improvement in WOF (35.5 MJ/m³) with 220% increment in comparison to pure Mg (Meenashisundaram and Gupta, 2015). In Table 2, AZ31B, AZ31B/0.66 vol%Al₂O₃, AZ31B/1.50 vol%Al₂O₃ and AZ31B/1.50 vol%Al₂O₃ nanocomposite prepared by DMD technique has been compared with pure Mg (Nguyen and Gupta, 2008). The inclusion of nanoparticles in the base matrix improved the 0.2% TYS (144 MPa), UTS (214 MPa) and ductility (29.5%) for pure Mg by 48%, 24% and 299% respectively. It is evident that in the case of an alloy, the matrix is composed of multiple elements when mixed with nanoparticles would significantly improve the mechanical tensile behavior for pure Mg. The tensile testing results of the Mg composites reinforced with 1.1 vol% Al₂O₃ (particle size 1 μm) (Hassan and Gupta, 2006) and 1.1 vol% Al₂O₃ (particle size 50 nm) (Hassan and Gupta, 2004) synthesized by the DMD technique were presented. The 0.2% TYS and UTS improved for both the composition while the ductility was substantially affected for 1.1 vol% Al₂O₃ (1 μm). It can be inferred that micron size reinforcements boost the 0.2% TYS and UTS properties of pure Mg but at the expense of ductility. Hence, the introduction of nanoreinforcements is an appealing key to elevate the tensile properties with the rise in ductility at room temperature for Mg-based matrix. Additionally, the adaption of solid based and liquid based processing technique to synthesize the nanocomposites helps in achieving uniform distribution of nanoparticles in Mg and Mg-alloy cooperated in benefiting tensile results.

Table 3 represents the tensile strength, ductility and work of fracture of the pure Mg and Mg/Y₂O₃ nanocomposite at different temperatures (Mallick *et al.*, 2010). It can be seen that the nanocomposite samples exhibit more than 20% higher TYS (except 250°C) compared to pure Mg sample at room temperature and elevated temperatures. Similarly, the higher UTS is observed in the composite sample as compared to pure Mg sample and their percentage was increased at the elevated temperatures. The results also exposed that the presence of nano-Y₂O₃ as reinforcement improved room temperature ductility in Mg. The tensile strength (TYS and UTS) in both the pure Mg and composite gradually decreased with the increase of test temperature. The thermally activated plastic deformation may be responsible for the smooth dislocation movement which tends to increase the percentage of elongation at the expense of tensile strength. As the material becomes softer at elevated temperature, the percentage of elongation in pure Mg samples predominantly increased with the increase of temperatures. However, comparatively less increase in the percentage of elongation with the rise in temperature can be seen in the composites. The thermally stable Y₂O₃ limits the movement of the material flow. Further, the interfacial bonding between the nanoparticle and the matrix may weaken at high temperatures. At all the test temperatures, higher work to fracture is observed in the composite sample.

Table 3 High temperature tensile properties of Mg-based nanocomposites synthesized by powder metallurgy method

Temperature	Materials	0.2% TYS (MPa)	UTS (MPa)	Ductility (%)	Work of fracture (MJ/m ³)
25°C	Pure Mg	197 ± 7	130 ± 8.8	8.0 ± 2.3	15.2 ± 2.7
	Mg/0.22Y ₂ O ₃	244 ± 12 (+ 24%)	146 ± 9 (+ 12%)	14 ± 2.1 (+ 75%)	23.1 ± 3.1 (+ 52%)
100°C	Pure Mg	110 ± 12	81 ± 11	26.5 ± 2.7	27.0 ± 3.4
	Mg/0.22Y ₂ O ₃	150 ± 10 (+ 36%)	95 ± 7.3 (+ 17%)	27.7 ± 2.5 (+ 5%)	33.1 ± 2.4 (+ 23%)
150°C	Pure Mg	96 ± 6	56 ± 6.5	31 ± 2.8	21 ± 3.7
	Mg/0.22Y ₂ O ₃	129 ± 4 (+ 34%)	90 ± 6.1 (+ 61%)	32 ± 1.9 (+ 3%)	32 ± 2.8 (+ 52%)
200°C	Pure Mg	75 ± 4	44 ± 4.6	34.1 ± 3.4	18 ± 2.9
	Mg/0.22Y ₂ O ₃	92 ± 7 (+ 23%)	68 ± 4.8 (+ 55%)	33.5 ± 2.0 (− 2%)	25 ± 2.6 (+ 38%)
250°C	Pure Mg	62 ± 4	38 ± 3	34.5 ± 2.2	15 ± 2.6
	Mg/0.22Y ₂ O ₃	73 ± 6 (+ 18%)	61 ± 5 (+ 61%)	24.5 ± 2.3 (− 29%)	16 ± 4.0 (+ 7%)

Note: Mallick, A., Tun, K.S., Vedantam, S., Gupta, M., 2010. Mechanical characteristics of pure Mg and a Mg/Y₂O₃ nanocomposite in the 25–250°C temperature range. *Journal of Materials Science* 45 (11), 3058–3066.

Further, a significant contribution to increasing the 0.2% TYS, UTS and ductility can be attributed to strengthening mechanisms: (a) Orowan Strengthening (b) Hall-Petch Strengthening (c) Forest Strengthening (d) Taylor Strengthening and (e) Load Transfer Effect. The in-depth details of these strengthening mechanism are as follows:

Orowan Strengthening

The formation of dislocation loops with high work-hardening rates around the nanoparticles as a result of obstruction put forward by the nanoparticles to the dislocation movement is termed as Orowan strengthening (Meenashisundaram and Gupta, 2016). The Orowan Strengthening equation is represented by:

$$\sigma_{\text{Orowan}} = \frac{0.13Gb}{\lambda} \ln \frac{r}{b} \quad (1)$$

where G , b and r are the shear modulus of Mg (17.3 GPa), Burgers vector of Mg (3.21×10^{-10}) and average radius. λ denotes interparticle spacing between the nanoparticles within the matrix and is denoted by:

$$\lambda = d_p \left[\left(\frac{1}{2V_p} \right)^{\frac{1}{3}} - 1 \right] \quad (2)$$

where V_p is the volume fraction of the reinforcements and d_p is the diameter of nanoparticles. Zhang and Chen (2008) in their work suggested that for metal matrix nanocomposites with decreasing size and increasing volume fraction of nanoparticles, the relative contribution of Orowan strengthening effect increases. Additionally, for activation of Orowan strengthening, the processing techniques need to be controlled the interparticle spacing to prevent agglomeration of nanoparticles in the magnesium matrix. It is recommended to incorporate till 2.5 vol% of nanoparticles in the matrix considering the ability of the processing techniques to disperse the nanoparticles throughout the matrix (Meenashisundaram et al., 2015b). Tun et al. (2010) in their work prepared Mg/(0.7Y₂O₃ + 0.3Cu) and Mg/(0.7Y₂O₃ + 0.6Cu) hybrid nanocomposites and monolithic Mg samples by powder metallurgy technique. Due to the fine dispersion of both Y₂O₃ and Cu nanoparticles in Mg, a significant increase in strength was noticed (Hassan and Gupta, 2002c). As seen from Table 1, the decrease in strength for Mg/(0.7Y₂O₃ + 0.6Cu) is due to the coarsening of copper clusters/agglomerates leading to a reduction in the Orowan strengthening effect. Similarly, Kumar et al. (2018a) also showed owing to the presence of GNPs, and there is a formation of residual loops resulting in high strain, thus strengthening the Mg-3Al/0.1GNP nanocomposite.

Hall-Petch Strengthening

The performance of grain size in executing the strength of the nanocomposite is defined as Hall-Petch Strengthening. The grain size can be related inversely to the strength of the material. Thus, when the grain size reduces the strength of the nanocomposite increases (Meenashisundaram et al., 2015b). The Hall Petch-equation is represented by:

$$\sigma_{\text{Hall-Petch}} = KD^{-0.5} \quad (3)$$

where K is the Hall Petch coefficient of Mg (280 MPa $\mu\text{m}^{1/2}$) and D represents the average grain size of the Mg composites. Moreover, the Zener equation illustrates the relationship amid nanoparticle size, the volume fraction of the nanoparticles and grain size of the nanocomposites and is represented by:

$$d_m = \frac{4\alpha d_p}{3v_p} \quad (4)$$

Earlier results show the grain size reduced for Mg/1.98TiO₂ and Mg/2.5TiO₂ nanocomposites prepared by powder metallurgy route in comparison to pure Mg by 12% and 18% respectively (Meenashisundaram *et al.*, 2015b). Similarly, the grain size also significantly reduced for Mg/1.98TiO₂ and Mg/2.5TiO₂ prepared by disintegrated melt deposition technique in comparison to pure Mg by 40% and 18% respectively (Meenashisundaram *et al.*, 2015b). Owing to significant grain reduction displayed by Mg/1.98TiO₂ and Mg/2.5TiO₂ nanocomposites prepared by powder metallurgy route and disintegrated melt deposition technique, the nanocomposites showed higher Hall-Petch strengthening of around 58 MPa and 61 MPa respectively. The results displayed increase in strength for Mg/1.98TiO₂ and Mg/2.5TiO₂ nanocomposites owing to uniformly dispersed TiO₂ nanoparticles acted as nucleation sites during recrystallization and pinned the grain boundaries thus reducing the grain size for pure Mg.

Forest Strengthening

The mismatch in the coefficient of thermal expansion (CTE) between the nanoparticles and the metal matrix is accommodated during material cooling and straining by the formation of geometrically necessary dislocations (GNDs), thus contributing to the strength of the composite (Tun and Gupta, 2007). The Forest Strengthening established from the relaxation of thermal stresses between the matrix and nanoreinforcements is represented by:

$$\sigma_{CTE} = A \cdot M \cdot G \cdot b \cdot \rho_{th}^{0.5} \quad (5)$$

$$\rho_{th} = 12 \frac{\sqrt{2} \cdot \Delta\alpha \cdot \Delta T \cdot f}{b \cdot d \cdot (1 - f)} \quad (6)$$

where A , ρ_{th} , $\Delta\alpha$, and ΔT are constants characterizing the transparency of the dislocation forest for basal-basal interaction in Mg (0.2), dislocation density, the difference in CTE values between the nanoparticles and pure Mg, and temperature excursion that is chosen to be 250K (for all the nanocomposite) assuming that the dislocation generation begins at 550K corresponding to a stress-free homologous temperature of 0.6.

Habibi *et al.* (2013) showed in their work that the coefficient of thermal expansion for magnesium and B₄C nanoparticles was ($28.9 \times 10^{-6} \text{ K}^{-1}$) and ($5.0 \times 10^{-6} \text{ K}^{-1}$) respectively. This considerable difference in coefficient of thermal expansion values, a large amount of geometrically necessary dislocations is awaited to build up at Mg/B₄C interface. Generally, micron-based composites contribute more to forest strengthening owing to the inclusion of higher volume percentage of reinforcements. This is not the case with nanocomposites as the inclusion of nanoparticles with more than 2.5 vol% would lead to clustering and agglomeration that are eventually reducing the strength of the nanocomposite. Tun *et al.* (2010) showed room temperature tensile test for Mg/(0.7Y₂O₃ + 0.3Cu) nanocomposites indicated increased dislocation density due to mismatch on the coefficient of thermal expansion for magnesium ($28.9 \times 10^{-6} \text{ K}^{-1}$), Y₂O₃ ($7.6 \times 10^{-6} \text{ K}^{-1}$) and copper ($18.3 \times 10^{-6} \text{ K}^{-1}$). However, with an increase in the volume percentage of Cu nanoparticles for Mg/(0.7Y₂O₃ + 0.6Cu) and Mg/(0.7Y₂O₃ + 0.6Cu) nanocomposites the tensile strength is seen to decrease gradually. The decrease in strength was attributed to increasing agglomeration of metallic Cu and Y₂O₃ nanoparticles.

Taylor Strengthening

The mismatch between the elastic modulus of the nanoparticle and magnesium matrix leading to the formation of geometrically necessary dislocations (GNDs) is termed as Taylor Strengthening. Taylor Strengthening is represented by:

$$\sigma_{EM} = \sqrt{3} \cdot \alpha \cdot G \cdot b \cdot \sqrt{\rho_{EM}} \quad (7)$$

$$\rho_{EM} = \frac{6V_p}{\pi d^3} \quad (8)$$

where α and ρ_{EM} are the constant (0.5) and dislocation density resulting from modulus mismatch.

Kumar *et al.* (2018a) reported an increase in dislocation density that due to misfit in elastic modulus values of GNPs (0.7–1.2 TPa), magnesium (40–45 GPa) and aluminum (69.6 GPa) respectively for Mg-3Al/0.1GNP nanocomposite. Similarly, Tun and Gupta (2007) in their work reported the difference of elastic modulus for magnesium (44.7 GPa) and yttria (177.6 GPa) and the higher volume fraction of reinforcement it would lead to higher dislocation density in the matrix. It can be inferred that the presence of nanoparticles causes incompatibility in deformation in the matrix through the geometrically necessary dislocations stored near the surfaces of particles. However, the Taylor strengthening doesn't contribute much to the nanocomposites in comparison to other strengthening mechanisms and hence is considered negligible.

Load Transfer Effect

The strengthening resulting from transferring of load from the soft matrix to the uniformly distributed hard and stiff nanoparticles under an external load thus contributing to the strength of the matrix is termed as load transfer effect (Zhong *et al.*, 2007). The Load Transfer Effect is represented by:

$$\sigma_{LT} = 0.5v_p\sigma_{Mg} \quad (9)$$

where σ_{LT} is the experimental 0.2% tensile yield strength (0.2% TYS) of pure Mg.

The transfer of load from the Mg matrix to the stiffer nanoparticles rely on the interfacial bonding between the matrix and nano-reinforcement. The FESEM micrographs, as shown in Fig. 2(a), indicates good interfacial bonding between the Mg-3Al alloy and GNP. Few cluster of GNP can be seen in Fig. 2(b). The hard nanoreinforcement restrict the grain growth by arresting the grain boundary migration. Furthermore, the intermetallic hard particles ($Mg_{17}Al_{12}$) that was formed during the development of an alloy of Mg and Al eventually improved the strength of nanocomposites by reducing the grain size (Mallick *et al.*, 2009). Since the incorporation of nano-reinforcements is in a lower amount, the load-bearing contribution for the nanocomposites can be considered negligible in comparison to micron-based composites. For example, magnesium reinforced with 10 vol% Ni50Ti50 and 40 vol% Ni50Ti50 exhibited a load transfer effect of 3.75 MPa and 15 MPa respectively (Meenashisundaram and Gupta, 2016).

The improvement in ductility for the magnesium matrix can be attributed to:

- (a) Presence of fine nanoparticulates; (b) Grain refinement; (c) Non-basal slip system or cross slip.

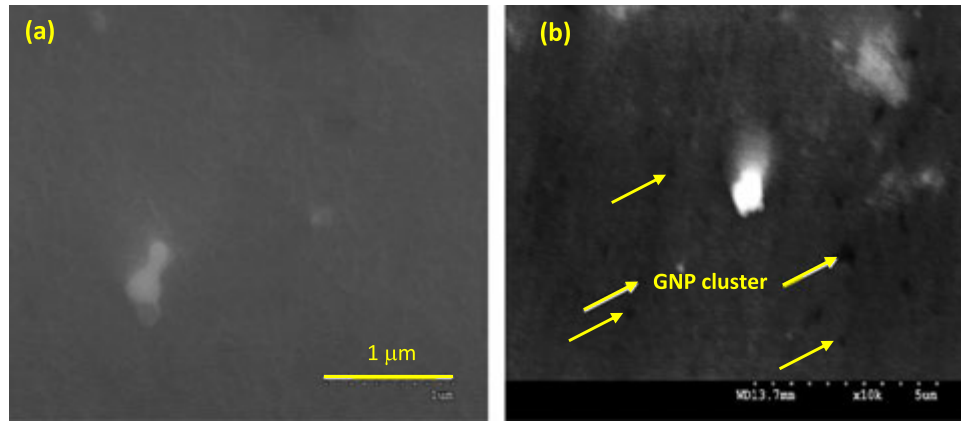


Fig. 2 The micrographs of Mg-3Al/0.5 CNT showing (a) interfacial integrity between CNT nano particle and Mg-3Al alloy matrix and (2) the presence of GNP cluster.

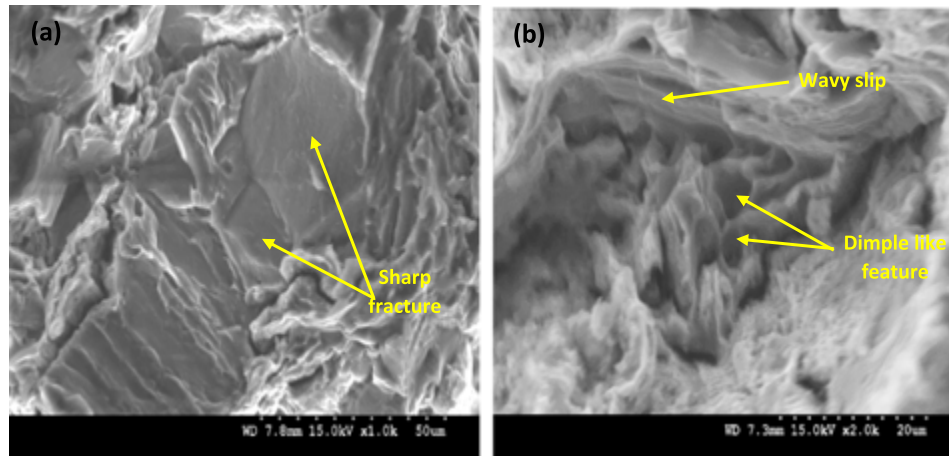


Fig. 3 Tensile fractograph confirming (a) brittle fracture in pure Mg and (b) mixed mode fracture with few dimples like features in Mg-2 wt% Y_2O_3 nanocomposite.

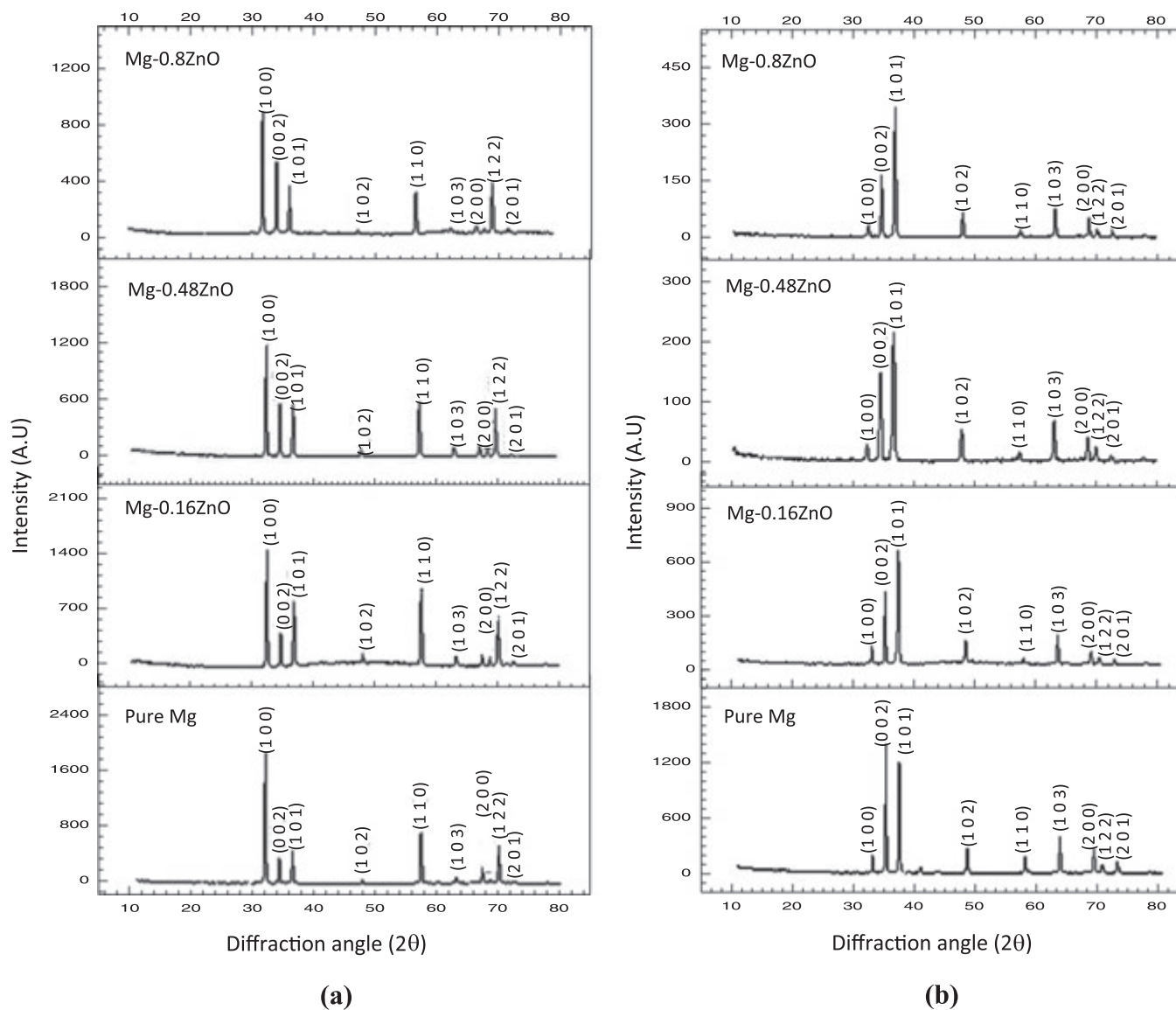


Fig. 4 X-ray diffractograms of pure Mg and Mg-ZnO nanocomposites were taken (a) along the cross-section of the samples and (b) along the longitudinal direction of the samples from Sankaranarayanan *et al.* Reproduced from Sankaranarayanan, S., Nayak, U.P., Sabat, R.K., *et al.*, 2014a. Nano-ZnO particle addition to monolithic magnesium for enhanced tensile and compressive response. *Journal of Alloys and Compounds* 615, 211–219.

The fine nanoparticulates in magnesium matrix:

- (1) Add locations to clear cleavage crack to an advancing crack front to dissipate stress concentration,
- (2) Alter the local effective stress from plane strain to plane stress state about the crack tip.

Mallick *et al.* (2010) reported the grain refinement in Mg/2 wt%Y₂O₃ nanocomposite which exhibited grain size of around 18 μm in comparison to the grain size of pure Mg (20 μm). The higher value of elastic modulus of the reinforcement compared to pure Mg significantly increase dislocation density. Further, this increase σ_{EM} and σ_{CTE} values which leading to increase the tensile strength in the composite. The reduction of grain size and the presence of dimples on fracture surfaces are also indicative of the improved tensile strength and ductility. Further, the tensile fractographs (Fig. 3(b)) confirmed the activation of non-basal slip systems. Additionally, there was a formation of wavy slip indicating homogeneous deformation and optimum ductility for Mg/2 wt%Y₂O₃ nanocomposite (Tun *et al.*, 2010).

This can primarily be attributed to: (a) the activation of non-basal slip system (Seetharaman *et al.*, 2013) and (b) tendency of Y₂O₃ particulates to enhance cross-slip (Tun *et al.*, 2013). In past studies, similar observations were made when Ti (Parande *et al.*, 2020), nanosize Al₂O₃ (Parande *et al.*, 2017) and carbon nanotube (Dyadyura and Sukhodub, 2017) were used as reinforcements. In past studies, it was also indicated that both precipitation and dispersion have the ability to enhance cross-slip tendency (Tun *et al.*, 2013).

Usually, the uniformly dispersed nanoparticles reduced the grain size of Mg by pinning the grain boundaries. These dispersed particles are supposed to add locations to clear cleavage crack ahead of an advancing crack front and expedite to weaken the stress concentration at the crack front. The fractographs confirmed the presence of intergranular cracks promoting an increase in ductility. Generally, Mg has a strong basal structure and its alignment of the basal planes (0002) parallel to the extrusion direction leads to poor ductility. With the incorporation of nano-reinforcements, the changes in crystallographic texture, as confirmed by X-Ray

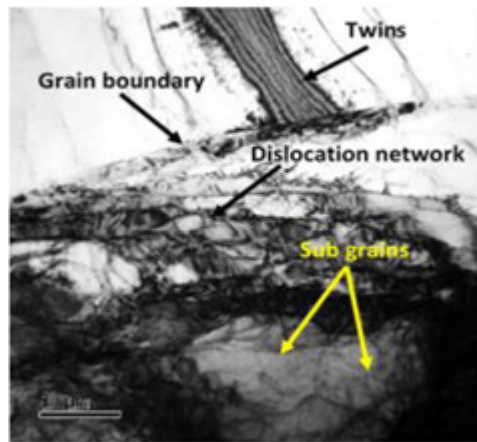


Fig. 5 Dislocation structures in Mg-3Al/0.3GO alloy-nanocomposite.

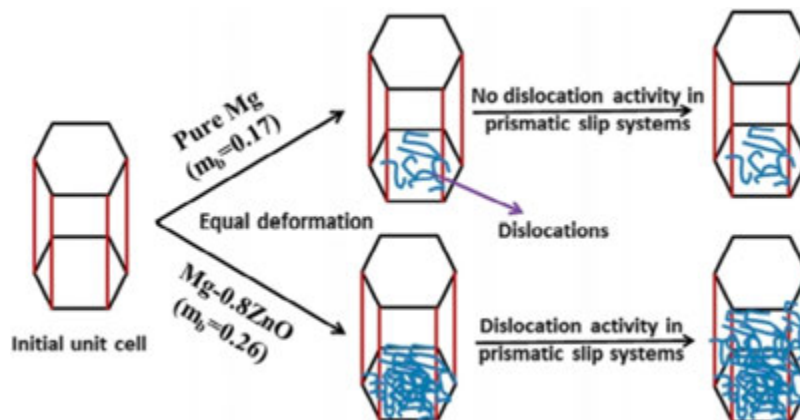


Fig. 6 Proposed schmid mechanism for mechanical property enhancement from Sankaranarayanan *et al.* Reproduced from Sankaranarayanan, S., Nayak, U.P., Sabat, R.K., *et al.*, 2014a. Nano-ZnO particle addition to monolithic magnesium for enhanced tensile and compressive response. Journal of Alloys and Compounds 615, 211–219.

diffraction studies, suggest the tilting of basal planes at an angle and not parallel to the extrusion direction. An example is in the case for Mg/ZnO nanocomposites synthesized by a disintegrated melt deposition method; the composites exhibited better fracture strain as compared to pure Mg (Sankaranarayanan *et al.*, 2014a). The X-ray diffractograms (Fig. 4) for Mg/ $x\%$ ZnO ($x = 0.16, 0.48, 0.8$) taken parallel to the extrusion direction indicated the highest intensity for $2\theta = 36^\circ$ corresponding to pyramidal plane conforming texture randomization.

The TEM observation of Mg-3%Al/0.3%GO alloy composite (Fig. 5) shows the presence of a dislocation network and the twins. This result reveals that GOs boosted in tilting of the basal plane from the extrusion direction and activating non-basal cross-slips. Similarly, Goh *et al.* (2008) confirmed in their work through TEM observations that CNTs boosted in tilting of the basal at an angle of 20° from the extrusion direction and activating non-basal cross-slips.

Further, to understand the texture effects on ductility enhancement through slip assisted hardening behavior, the Schmid factor (Fig. 6) was proposed by Sankaranarayanan *et al.* (2014a). Schmid factor is the measure of volume fraction of grains contributing to each slip system suggesting more dislocation activity was carried out along basal planes. This in turn would increase the apparent critical resolved shear stress (CRSS) value in the basal plane for further dislocation activity. Additionally, the nanoparticles interactions with the dislocations aid in boosting the hardening behavior and lead to increment in CRSS value closer to that of the prismatic slip system.

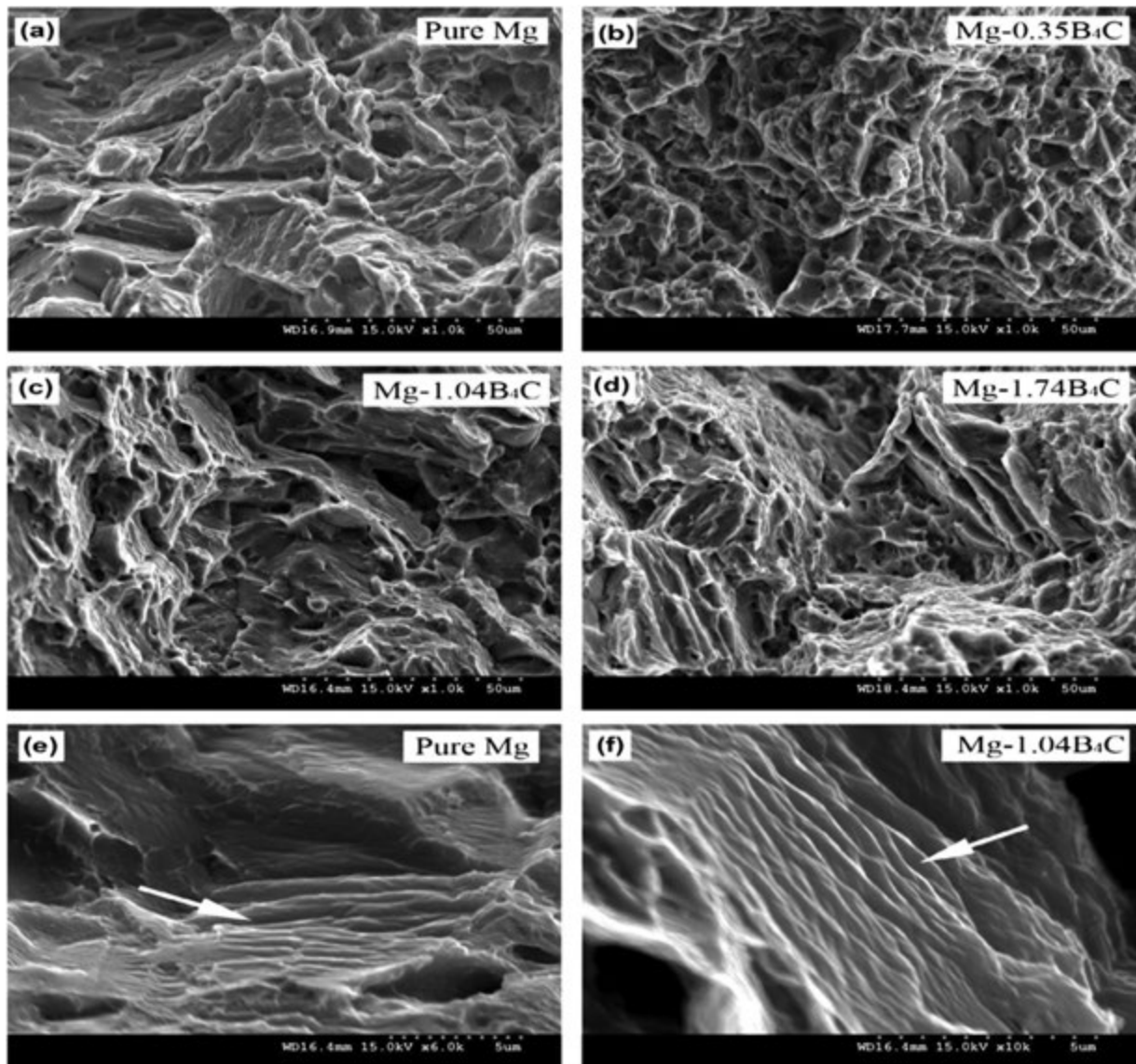


Fig. 7 Tensile fracture surface of (a) pure Mg, (b) Mg/0.35B₄C; (c) Mg/1.04B₄C; (d) Mg/1.74B₄C; (e) presence of slip in basal plane and (f) combined effect of basal and non-basal slip in Mg/1.04B₄C nanocomposite from Sankaranarayanan *et al.* Reproduced from Sankaranarayanan, S., Sabat, R.K., Jayalakshmi, S., Suwas, S., Gupta, M., 2014b. Effect of nanoscale boron carbide particle addition on the microstructural evolution and mechanical response of pure magnesium. *Materials & Design* 2014 (56), 428–436.

Also, the work of fracture (WOF) was seen to improve with the addition of nanoparticles. In the case of Mg/0.5Al nanocomposites the WOF improved by 119% (Tun and Gupta, 2007). The significant improvement in the work of fracture is due to simultaneous improvement in the strength and ductility of the nanocomposite.

From the fracture analysis, Fig. 7 (a) shows Magnesium's inability to deform homogeneously under uniaxial tensile loading was evident through the presence of cleavage steps and small plastic deformation with reasonably sharp fractures surfaces. Fig. 7 (b)-(d) show ductile fracture owing to plastic deformation. Further, there is a combined effect of basal and non-basal slip as imposed by uniformly dispersed B₄C nanoparticles on pure Mg (Sankaranarayanan *et al.*, 2014b).

Acknowledgment

The authors acknowledge and are grateful to Elsevier for allowing them to reproduce some images in this article.

References

- Alam, M.E., Han, S., Nguyen, Q.B., Hamouda, A.M.S., Gupta, M., 2011. Development of new magnesium based alloys and their nanocomposites. *Journal of Alloys and Compounds* 509 (34), 8522–8529.
- Casati, R., Vedani, M., 2014. Metal matrix composites reinforced by nano-particles – A review. *Metals* 4 (1), 65–83.
- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2017a. Ex situ production routes for metal matrix nanocomposites. In *Aluminum and Magnesium Metal Matrix Nanocomposites*. Springer. pp. 19–40.
- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2017b. Metal matrix nanocomposites: An overview. In *Aluminum and Magnesium Metal Matrix Nanocomposites*. Springer. pp. 1–17.
- Dyadyura, K., Sukhodub, F., 2017. Magnesium-based matrix composites reinforced with nanoparticles for biomedical applications. In: *Proceedings of the 7th International Conference Nanomaterials: Application & Properties (NAP)*, IEEE.
- Gehrmann, R., Frommert, M.M., Gottstein, G., 2005. Texture effects on plastic deformation of magnesium. *Materials Science and Engineering A* 395 (1–2), 338–349.
- Goh, C., Wei, J., Lee, L.C., Gupta, M., 2007. Properties and deformation behaviour of Mg–Y₂O₃ nanocomposites. *Acta Materialia* 55 (15), 5115–5121.
- Goh, C., Wei, J., Lee, L.C., Gupta, M., 2008. Ductility improvement and fatigue studies in Mg–CNT nanocomposites. *Composites Science and Technology* 68 (6), 1432–1439.
- Goh, C.S., Wei, J., Lee, L.C., Gupta, M., 2006. Simultaneous enhancement in strength and ductility by reinforcing magnesium with carbon nanotubes. *Materials Science and Engineering A* 423 (1–2), 153–156.
- Gupta, M., Ling, S.N.M., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites*. John Wiley & Sons.
- Gupta, M., Wong, W., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.
- Gupta, M., Lai, M., Saravananarathan, D., 2000. Synthesis, microstructure and properties characterization of disintegrated melt deposited Mg/SiC composites. *Journal of Materials Science* 35 (9), 2155–2165.
- Habibi, M.K., Hamouda, A.S., Gupta, M., 2013. Hybridizing boron carbide (B₄C) particles with aluminum (Al) to enhance the mechanical response of magnesium based nanocomposites. *Journal of Alloys and Compounds* 550, 83–93.
- Hassan, S., Gupta, M., 2002a. Development of ductile magnesium composite materials using titanium as reinforcement. *Journal of Alloys and Compounds* 345 (1–2), 246–251.
- Hassan, S., Gupta, M., 2002b. Development of high strength magnesium based composites using elemental nickel particulates as reinforcement. *Journal of Materials Science* 37 (12), 2467–2474.
- Hassan, S., Gupta, M., 2002. Development of a novel magnesium–copper based composite with improved mechanical properties. *Materials Research Bulletin* 37 (2), 377–389.
- Hassan, S., Gupta, M., 2004. Development of high performance magnesium nanocomposites using solidification processing route. *Materials Science and Technology* 20 (11), 1383–1388.
- Hassan, S., Gupta, M., 2006. Effect of particulate size of Al₂O₃ reinforcement on microstructure and mechanical behavior of solidification processed elemental Mg. *Journal of alloys and compounds* 419 (1–2), 84–90.
- Hassan, S., Gupta, M., 2007a. Development of nano-Y₂O₃ containing magnesium nanocomposites using solidification processing. *Journal of Alloys and Compounds* 429 (1–2), 176–183.
- Hassan, S., Gupta, M., 2007b. Effect of nano-ZrO₂ particulates reinforcement on microstructure and mechanical behavior of solidification processed elemental Mg. *Journal of composite materials* 41 (21), 2533–2543.
- Hassan, S., Gupta, M., 2008. Effect of submicron size Al₂O₃ particulates on microstructural and tensile properties of elemental Mg. *Journal of alloys and compounds* 457 (1–2), 244–250.
- Hassan, S., Ogunlakin, N.O., Aqeeli-Al, N., *et al.*, 2018. Development of tensile-compressive asymmetry free magnesium based composite using TiO₂ nanoparticles dispersion. *Journal of Materials Research* 33 (2), 130–137.
- Ho, K., Gupta, M., Srivatsan, T.S., 2004. The mechanical behavior of magnesium alloy AZ91 reinforced with fine copper particulates. *Materials Science and Engineering A* 369 (1–2), 302–308.
- Jayalakshmi, S., Loh, Z., Seetharaman, S., Hamouda, A.S., Gupta, M., 2012. Microstructure and mechanical properties of Mg–5Nb metal-metal composite reinforced with nano SiC ceramic particles. *Metals* 2 (2), 178–194.
- Kaiser, F., Kainer, K., 2003. *Magnesium Alloys and Technology*. John Wiley & Sons.
- Kujur, M.S., Mallick, A., Manakari, V., *et al.*, 2017. Significantly enhancing the ignition/compression/damping response of monolithic magnesium by addition of Sm₂O₃ nanoparticles. *Metals* 7 (9), 357. (1–16).
- Kujur, M.S., Manakari, V., Parande, G., *et al.*, 2018. Enhancement of thermal, mechanical, ignition and damping response of magnesium using nano-ceria particles. *Ceramics International* 44 (13), 15035–15043.
- Kujur, M.S., Manakari, V., Parande, G., *et al.*, 2019. Role of rare earth oxide reinforcements in enhancing the mechanical, damping and ignition resistance of magnesium. In: Srivatsan, T.S., Gupta, M. (Eds.), *Nanocomposites VI: Nanoscience and Nanotechnology in Advanced Composites*. Springer, pp. 115–124.
- Kumar, P., Kujur, M.S., Mallick, A., Tun, K.S., Gupta, M., 2018a. Effect of graphene nano-platelets on the mechanical properties of Mg/3wt% Al alloy-nanocomposite. *IOP Conference Series: Materials Science and Engineering* 346 (1).
- Kumar, P., Mallick, A., Kujur, M.S., *et al.*, 2018b. Strength of Mg–3% Al alloy in presence of graphene nano-platelets as reinforcement. *Materials Science and Technology* 34 (9), 1086–1095.
- Mallick, A., Vedantam, S., Lu, L., 2009. Grain size dependent tensile behavior of Mg–3% Al alloy at elevated temperatures. *Materials Science and Engineering A* 515 (1–2), 14–18.

- Mallik, A., Tun, K.S., Vedantam, S., Gupta, M., 2010. Mechanical characteristics of pure Mg and a Mg/Y₂O₃ nanocomposite in the 25–250°C temperature range. *Journal of Materials Science* 45 (11), 3058–3066.
- Meenashisundaram, G., Gupta, M., 2016. Emerging environment friendly, magnesium-based composite technology for present and future generations. *JOM* 68 (7), 1890–1901.
- Meenashisundaram, G.K., Gupta, M., 2014. Low volume fraction nano-titanium particulates for improving the mechanical response of pure magnesium. *Journal of Alloys and Compounds* 593, 176–183.
- Meenashisundaram, G.K., Gupta, M., 2015. Synthesis and characterization of high performance low volume fraction TiC reinforced Mg nanocomposites targeting biocompatible/structural applications. *Materials Science and Engineering A* 627, 306–315.
- Meenashisundaram, G.K., Seetharaman, S., Gupta, M., 2014. Enhancing overall tensile and compressive response of pure Mg using nano-TiB₂ particulates. *Materials Characterization* 94, 178–188.
- Meenashisundaram, G.K., Nai, M.H., Almajid, A., Gupta, M., 2015a. Development of high performance Mg–TiO₂ nanocomposites targeting for biomedical/structural applications. *Materials & Design* 65, 104–114.
- Meenashisundaram, G.K., Nai, M.H., Gupta, M., 2015b. Effects of primary processing techniques and significance of hall-petch strengthening on the mechanical response of magnesium matrix composites containing TiO₂ nanoparticulates. *Nanomaterials* 5 (3), 1256–1283.
- Meenashisundaram, G.K., Nai, M.H., Almajid, A., Gupta, M., 2016. Reinforcing low-volume fraction nano-TiN particulates to monolithic, pure Mg for enhanced tensile and compressive response. *Materials* 9 (3), 134.
- Meenashisundaram, G.K., Ong, T.H.D., Parande, G., 2017. Using lanthanum to enhance the overall ignition, hardness, tensile and compressive strengths of Mg–0.5 Zr alloy. *Journal of Rare Earths* 35 (7), 723–732.
- Nguyen, Q., Gupta, M., 2008. Increasing significantly the failure strain and work of fracture of solidification processed AZ31B using nano-Al₂O₃ particulates. *Journal of Alloys and Compounds* 459 (1–2), 244–250.
- Paramsothy, M., Chan, J., Kwok, R., Gupta, M., 2011. Addition of CNTs to enhance tensile/compressive response of magnesium alloy ZK60A. *Composites Part A Applied Science and Manufacturing* 42 (2), 180–188.
- Parande, G., Manakari, V., Wakeel, S., *et al.*, 2018. Enhancing mechanical response of monolithic magnesium using nano-NiTi (Nitinol) particles. *Metal* 8 (12), 1014.
- Parande, G., Manakari, V., Prasad, S., *et al.*, 2020. Strength retention, corrosion control and biocompatibility of Mg–Zn–Si/HA nanocomposites. *Journal of the Mechanical Behavior of Biomedical Materials* 103, 103584.
- Parande, G., Manakari, V., Meenashisundaram, G.K., Gupta, M., 2017. Enhancing the tensile and ignition response of monolithic magnesium by reinforcing with silica nanoparticulates. *Journal of Materials Research* 32 (11), 2169–2178.
- Sankaranarayanan, S., Nayak, U.P., Sabat, R.K., *et al.*, 2014a. Nano-ZnO particle addition to monolithic magnesium for enhanced tensile and compressive response. *Journal of Alloys and Compounds* 615, 211–219.
- Sankaranarayanan, S., Sabat, R.K., Jayalakshmi, S., Suwas, S., Gupta, M., 2014b. Effect of nanoscale boron carbide particle addition on the microstructural evolution and mechanical response of pure magnesium. *Materials & Design* 2014 56, 428–436.
- Sankaranarayanan, S., Sabat, R.K., Jayalakshmi, S., *et al.*, 2015. Mg/BN nanocomposites: Nano-BN addition for enhanced room temperature tensile and compressive response. *Journal of Composite Materials* 49 (24), 3045–3055.
- Seetharaman, S., Jayalakshmi, S., Gupta, M., Hamouda, A.S., 2012. Influence of micron-Ti and nano-Cu additions on the microstructure and mechanical properties of pure magnesium. *Metals* 2 (3), 274–291.
- Seetharaman, S., Jayalakshmi, S., Tun, K.S., Hamouda, A.M.S., Gupta, M., 2013. Synthesis and characterization of nano boron nitride reinforced magnesium composites produced by the microwave sintering method. *Materials* 6 (5), 1940–1955.
- Tjong, S.C., 2007. Novel nanoparticle-reinforced metal matrix composites with enhanced mechanical properties. *Advanced Engineering Materials* 9 (8), 639–652.
- Tun, K., Wong, W.L.E., Nguyen, Q.B., Gupta, M., 2013. Tensile and compressive responses of ceramic and metallic nanoparticle reinforced Mg composites. *Materials* 6 (5), 1826–1839.
- Tun, K.S., Gupta, M., 2007. Improving mechanical properties of magnesium using nano-yttria reinforcement and microwave assisted powder metallurgy method. *Composites Science and Technology* 67 (13), 2657–2664.
- Tun, K.S., Gupta, M., 2009. Development of magnesium/(yttria + nickel) hybrid nanocomposites using hybrid microwave sintering: Microstructure and tensile properties. *Journal of Alloys and Compounds* 487 (1–2), 76–82.
- Tun, K.S., Gupta, M., Srivatsan, T., 2010. Investigating influence of hybrid (yttria + copper) nanoparticle reinforcements on microstructural development and tensile response of magnesium. *Materials Science and Technology* 26 (1), 87–94.
- Tun, K.S., Jayaramanvar, P., Nguyen, Q.B., *et al.*, 2012. Investigation into tensile and compressive responses of Mg–ZnO composites. *Materials Science and Technology* 28 (5), 582–588.
- Wakeel, S., Manakari, V., Parande, G., *et al.*, 2018. Synthesis and mechanical response of NiTi SMA nanoparticle reinforced Mg composites synthesized through microwave sintering process. *Materials Today Proceedings* 5 (14), 28203–28210.
- Wong, W., Gupta, M., 2016. High performance lightweight magnesium nano composites for engineering and biomedical applications. *Nano World Journal* 2, 78–83.
- Wong, W., Gupta, M., 2017. Development of Mg/Cu nanocomposites using microwave assisted rapid sintering. *Composites Science and Technology* 67 (7–8), 1541–1552.
- Wong, W.L.E., Gupta, M., 2006. Simultaneously improving strength and ductility of magnesium using nano-size SiC particulates and microwaves. *Advanced Engineering Materials* 8 (8), 735–740.
- Xiang, S., Gupta, M., Wang, X.J., *et al.*, 2017. Enhanced overall strength and ductility of magnesium matrix composites by low content of graphene nanoplatelets. *Composites Part A Applied Science and Manufacturing* 100, 183–193.
- Zhang, Z., Chen, D., 2008. Contribution of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites. *Materials Science and Engineering A* 483, 148–152.
- Zhong, X., Wong, W., Gupta, M., 2007. Enhancing strength and ductility of magnesium by integrating it with aluminum nanoparticles. *Acta Materialia* 55 (18), 6338–6344.

Tensile Response of Al-Based Nanocomposites

Penchal Reddy Matli, Vyasaraj Manakari, Gururaj Parande, and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Transportation sector (land, air, and water) is the main sector where lightweight metallic materials are actively sought to reduce fossil fuel consumption. In this context, metal matrix composites (MMCs) are receiving increased consideration primarily for reducing the carbon signature and ever increasing global warming (Venci and Rac, 2004; Chawla and Chawla, 2006).

In the 21st century, high strength, lightweight and energy-efficient materials have received extensive attention, since the problems of energy and environment are major concern areas. In order to circumvent these issues, researchers and engineers are striving to develop new engineering materials such as metal based nanocomposites that can satisfy both global and engineers' concerns (Fig. 1). These modern engineering materials are expected to find wide spectrum of applications in multiple engineering sectors such as aerospace, defense, automobile and electronic industries (Mathew *et al.*, 2018).

The performance and efficiency of these applications can be increased largely by the application of modern engineering materials: composites. Metal matrix composites are a unique class of materials that are targeted to cater to ever increasing stringent service conditions to improve reliability and product/device lifetime. Hence, technological developments in various fields depend on the advances made in the field of materials and in a way, it is one of the key factors that ultimately decide the extent of perfection and sophistication required by modern technology.

Metal matrix composites have the capability to integrate the unique capabilities of judiciously selected reinforcement in the form of particles, whiskers or short/continuous fibers with that of the matrix (Ibrahim *et al.*, 1991; Lloyd, 1994). In light metal matrix composites, Al, Mg, and Ti are commonly used as base metallic matrix and ceramic particles (oxides, carbides, borides, and nitrides) are generally used as the reinforcing phases. The main role of the reinforcement is to increase the strength, stiffness and thermal capabilities while reducing the thermal expansion coefficient of the resulting MMC. However, the choice of an appropriate matrix needs careful consideration to avoid undesirable chemical reactions between the matrix and the reinforcement (Ma *et al.*, 1996; Kang and Chan, 2004).

Nanocomposites, a variation of conventional MMCs, are largely targeted for automotive and aerospace industries due to their ability to resist high temperatures and pressures. Recently, metal matrix nanocomposites (MMNCs) have become more attractive in various applications due to their superior mechanical properties when compared to conventional MMCs containing micro-particles. Nanocomposites are composite material that display at least one of its matrix feature such as grain size or reinforcement length scale in nanometric zone that is typically less than 100 nm (Rino *et al.*, 2012; Abbass and Fouad, 2014; Babalola *et al.*, 2014).



Fig. 1 Metal matrix nanocomposites for different applications.

Aluminum is one of the lightest structural metallic material (with a density of 2.7 gm/cm^3 , about a third that of steel) that is widely available and has attracted much attention for weight-critical applications in automotive, aerospace, space, sports and electronic industries, due to its high ductility, appreciable corrosion resistance and attractive strength/weight ratio (Ipek, 2005; Topcu *et al.*, 2009; El-Labban *et al.*, 2014). Depending on the desired application, both micron and nano length scale particles can be used as a reinforcing phase in the metal matrix (Fogagnolo *et al.*, 2003). Nanoparticles as reinforcement in metal matrix composites have been progressively replacing other types of reinforcement such as nanofibers, nanowhiskers, or nanoplatelets due their ease of manufacture and comparatively low cost. The most commonly used types of nanoparticles are SiC, TiC, B_4C , Si_3N_4 , SiO_2 , AlN, Al_2O_3 , graphene nanoparticles, amongst others (Karbalaee Akbari *et al.*, 2013; Pradhan *et al.*, 2015; Bisht *et al.*, 2017; Issa *et al.*, 2017; Matli *et al.*, 2017b; Reddy *et al.*, 2017; Ubaid *et al.*, 2017; Reddy *et al.*, 2018a).

Aluminum alloys have been developed progressively over last 100 years and utilized significantly in engineering applications over last 40 years. They exhibit wide spectrum of properties and cater to a wide array of applications. Integrating these aluminum alloys with reinforcements at nanolength scale provide the unlimited possibility of tailoring their end properties for even a wider array of applications and for more abusive conditions. This unique ability of end application based tailoring of properties and other attributes like ease of manufacturing, high strength, low coefficient of thermal expansion, wear resistance, corrosion resistance, durability, adaptability, and cost of effectiveness, etc., have been catalytic in attracting the attention of many industries towards using aluminum matrix nanocomposites in several engineering application (Fig. 2) (Rawal, 2001; Miracle, 2005).

Several manufacturing methods have been used to produce Al-based nanocomposites and these include powder metallurgy (Zakaria, 2014), conventional casting (Singh *et al.*, 2015) and conventional hot extrusion (El-Kady and Fathy, 2014). The main disadvantage of the conventionally processed materials is a lack of homogeneity in the dispersion of the particles and poor interfacial integrity between the matrix and the particles. However, research and development on compositional adjustment of nanocomposites and the methods to make them are still ongoing not only to overcome these limitations but also to realize overall superior microstructural characteristics.

Generally, the powder metallurgy (PM) process is widely known to be an excellent metallic material synthesis technique including that for composites (Reddy *et al.*, 2017). It usually involves mixing of powders of the matrix elements with the reinforcing particles, followed by compaction and solid-state sintering. Most powder consolidation and other processing steps including sintering are carried out below the matrix solidus temperature.



Fig. 2 Applications of aluminum nanocomposites in various sectors.

In addition to traditionally used sintering, microwave sintering using a 2.45 GHz microwave furnace is also successfully and economically used to sinter the compacted materials. The frequency of these microwave electromagnetic waves ranges from 400 MHz to 60 GHz. Microwave susceptors are normally used to aid the sintering process as they rapidly couple with microwaves and enable rapid heating of the compacted powder to be sintered. These susceptors are often made of silicon carbide. The microwave heating presents a potential economical sintering process with shortened processing time for the materials leading to cost, time and energy savings. This method is expected to overcome many of the shortcomings of the conventional sintering process such as maintaining comparatively refined microstructure (Yang *et al.*, 2004; Matli *et al.*, 2016).

The sintered composites are sometimes subjected to secondary processing such as extrusion to reduce porosity, refine the microstructure, and to homogenize the distribution of the reinforcement, all of which tend to improve the mechanical properties of materials which involve high temperatures and large strain deformation (Suresh *et al.*, 1993; Clyne and Withers, 1995).

In view of tremendous potential of nanocomposites in engineering applications, this article attempts to provide a comprehensive overview of the techniques used for manufacturing metal matrix nanocomposites with particular emphasis on mechanical properties including hardness and tensile properties.

Processing Techniques

Among the many factors, the properties of the composites critically depend on the effectiveness of the synthesis techniques to disperse the reinforcements uniformly within the metallic matrix. Metal matrix nanocomposites are typically synthesized using either solid-based processing (powder metallurgy) or liquid-based techniques (sand casting, permanent mold casting, disintegrated melt deposition, pressure infiltration, squeeze casting etc.). Technical difficulties related to liquid state processing include residual porosity, reinforcement segregation, and clustering and poor interfacial bonding which adversely affect the properties of the composites. Powder metallurgy processing can circumvent many of these drawbacks (heterogeneity in microstructure and reinforcement distribution) and particularly limit the undesired reaction between the metallic matrix and reinforcement because of lower temperatures (lower than melting point of base matrix) utilized during various processing steps. Hence, the discussion in subsequent sections will be limited to powder metallurgy technique incorporating hybrid microwave sintering that was developed by our research group. Detailed information on this processing technique can be found in open literature (Reddy *et al.*, 2018b).

Powder metallurgy technique assisted with hybrid microwave sintering (PM + MW).

Powder metallurgy process is divided into several steps including powder preparation, mixing, consolidation and sintering. Fig. 3 presents a general flow chart for the powder metallurgy process.

Typically matrix in powder form and nano-size reinforcements are carefully weighed and blended to obtain homogeneously mixed powders. These powders are compacted (uniaxially/hot isostatic pressing) to obtain a green compact billets. This green compact is further sintered for a pre-determined time using a conventional furnace or a microwave furnace.

After primary processing, billets of microwave sintered Al and Al composites are hot worked using methods such as extrusion, forging and rolling. Depending on the materials system, secondary processing can be done either below or above recrystallization temperature. Fig. 3 shows a typical processing methodology for Al-BN metal matrix nanocomposites. Characterization studies are typically carried out either on sintered or secondary processed samples using international standards.

Properties of Al-Based Metal Matrix Nanocomposites

Aluminum can be reinforced with suitable reinforcement to improve its properties such as specific strength, stiffness, hardness, and wear resistance. Pure aluminum has been studied extensively because of its low density, good machinability, high ductility, good thermal stability, and other salient properties. The use of aluminum has been growing in the industry as a material for several versatile and typically weight critical applications. Commonly used nanoreinforcements such as Al_2O_3 , B_4C , SiC, BN, TiC, SiO_2 , etc., have noticeably influenced the structural, physical and mechanical properties of Al-based nanocomposites.

Reddy *et al.* (2018b) investigated BN nanoparticles reinforced Al metal matrix composites with volume fraction ranging from 0 to 1.5 vol%. These composites were synthesized using the blend-press-sinter powder metallurgy technique followed by hot extrusion. The experimental results showed that the density decreases while porosity increases with the addition of BN nanoparticles (Fig. 4). This can be ascribed to the lower density of nanosized boron nitride particles (2.1 g/cc) when compared to pure aluminum (2.7 g/cc).

Toozandehjani *et al.* (2017) synthesized Al-5 wt% Al_2O_3 nanocomposite using ball milling assisted powder metallurgy technique. Aluminum and spherical nano alumina (Al_2O_3) particles were ball milled in planetary ball milling machine at 300 rpm with 8:1 ball to powder ratio for different milling times ranging from 0.5 to 12 h. The ball milled powder mixtures were uniaxially compacted at a pressure of 150 MPa and sintered at 580°C for 45 min to produce nanocomposites. The results of X-ray diffraction studies are shown in Fig. 5. The fewer and low intensity peaks of alumina may be attributed to its low volume fraction (Prabhu *et al.*, 2006).

Reddy *et al.* (2017) investigated the effect of SiC content (0.3, 0.5, 1.0, and 1.5 vol%) on the microstructural characteristics of Al nanocomposites fabricated by microwave sintering followed by hot extrusion. Fig. 6 shows the XRD patterns of Al-SiC nanocomposites. Results revealed the presence of SiC in the Al matrix with no signs of the formation of other intermetallic phases.

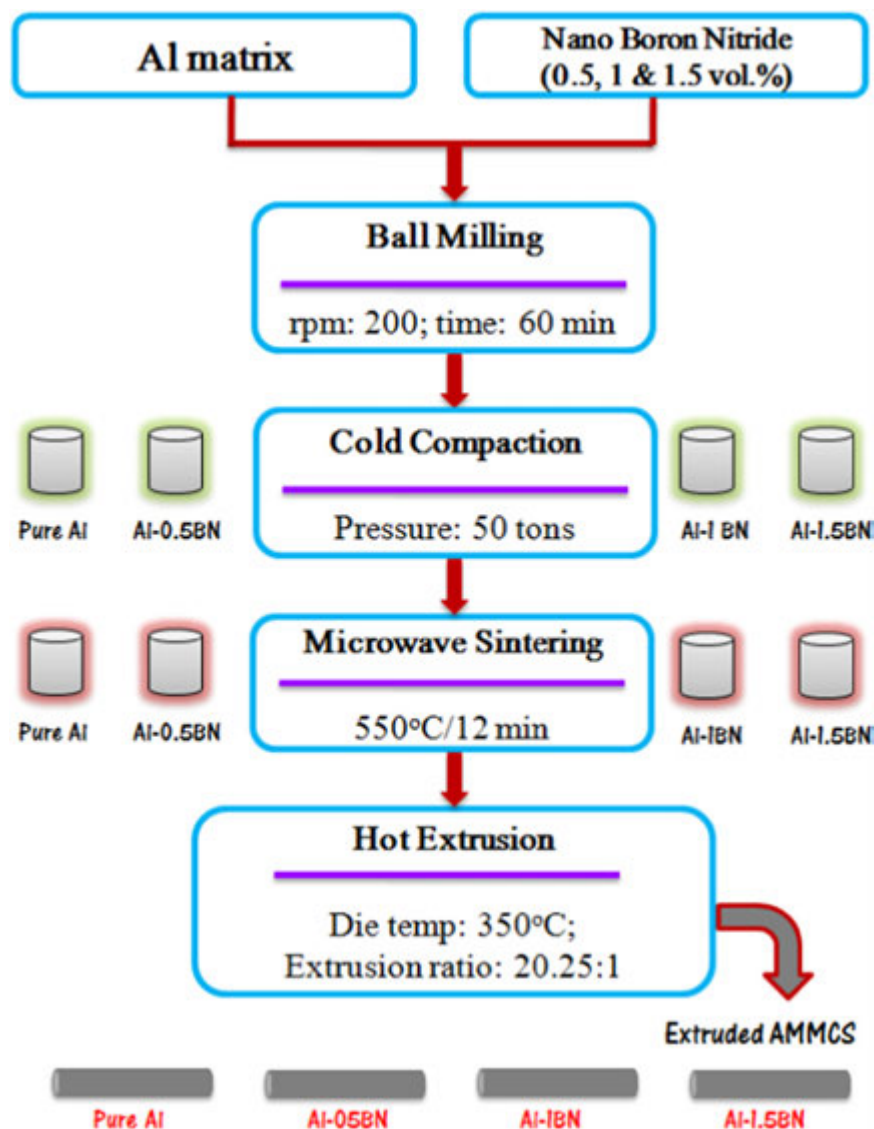


Fig. 3 Flow-chart of fabrication of Al-BN nanocomposites. Reproduced from Reddy, M.P., *et al.*, 2018b. Enhancing compressive, tensile, thermal and damping response of pure Al using BN nanoparticles. *Journal of Alloys and Compounds* 762, 398–408.

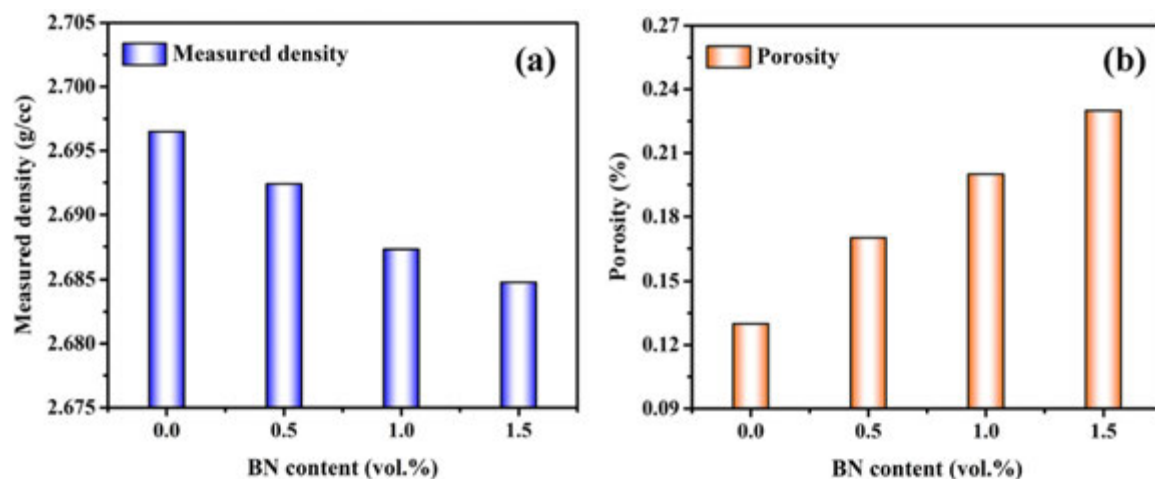


Fig. 4 Variation of density (a) and porosity (b) of the extruded Al-BN nanocomposites. Reproduced from Reddy, M.P., *et al.*, 2018b. Enhancing compressive, tensile, thermal and damping response of pure Al using BN nanoparticles. *Journal of Alloys and Compounds* 762, 398–408.

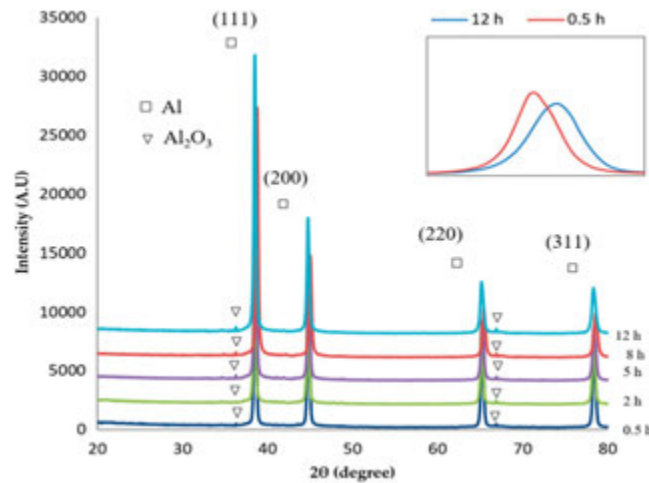


Fig. 5 XRD spectra of Al-5Al₂O₃ nanocomposite powders milled for different times. Reproduced from Toozandehjani, M., *et al.*, 2017. Effect of milling time on the microstructure, physical and mechanical properties of Al-Al₂O₃ nanocomposite synthesized by ball milling and powder metallurgy. Materials 10 (11), 1232.

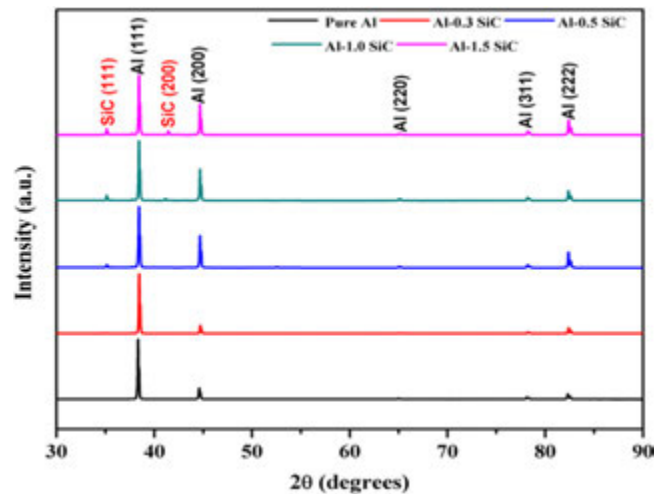


Fig. 6 XRD patterns of pure Al and Al-SiC nanocomposites. Reproduced from Reddy, M.P., *et al.*, 2017. Enhanced performance of nano-sized SiC reinforced Al metal matrix nanocomposites synthesized through microwave sintering and hot extrusion techniques. Progress in Natural Science: Materials International 27 (5), 606–614.

Fig. 7 shows optical micrographs of aluminum nanocomposites containing Al₂O₃ and SiC nanoparticulates. The authors (Mahmoud *et al.*, 2012) reported an increase in the agglomeration of nanoparticulates when the volume fraction of the nanoparticulates dispersed into the Al matrix is increased. The Al-SiC nanocomposites exhibited more agglomeration percent when compared with the Al-Al₂O₃ nanocomposites. The agglomerations size in Al-SiC nanocomposites was found to vary between 0.5 and 10 μm .

Issa *et al.* (2017) reported the fabrication and mechanical properties of SiO₂ nanoparticles (1, 2, and 3 wt%) reinforced aluminum matrix composites using powder metallurgy and hot extrusion processes. The SEM microstructural examination of extruded Al-SiO₂ composite samples is shown in **Fig. 8**. Results revealed non-uniform distribution of SiO₂ nanoparticles that was particularly attributed to their nanometric size. To note that dispersion of nanoparticles is always challenging due to their large surface area that promotes clustering.

Matli *et al.* (2017b) fabricated Al-Si₃N₄ (0, 5, 1, and 1.5 vol%) nanocomposites using the powder metallurgy method involving microwave sintering technique followed by hot extrusion. The authors reported homogeneous distribution of Si₃N₄ nanoparticles in the Al matrix validated through the elemental distribution map secured through SEM/EDS set-up. EDS analyses in **Fig. 9**, confirmed the presence of Si and N phases and were in good agreement with the distribution of Si₃N₄ in the Al matrix.

Li *et al.* (2019) investigated the mechanical behavior of 10 vol% SiC/Al nanocomposites. The nanocomposites were synthesized by hot pressure sintering and hot extrusion techniques. TEM micrographs in **Fig. 10** show morphology of the Al grains in extruded 10 vol% SiC/Al nanocomposite. The distribution of nano-sized SiC particle reinforcement in matrix was good due to

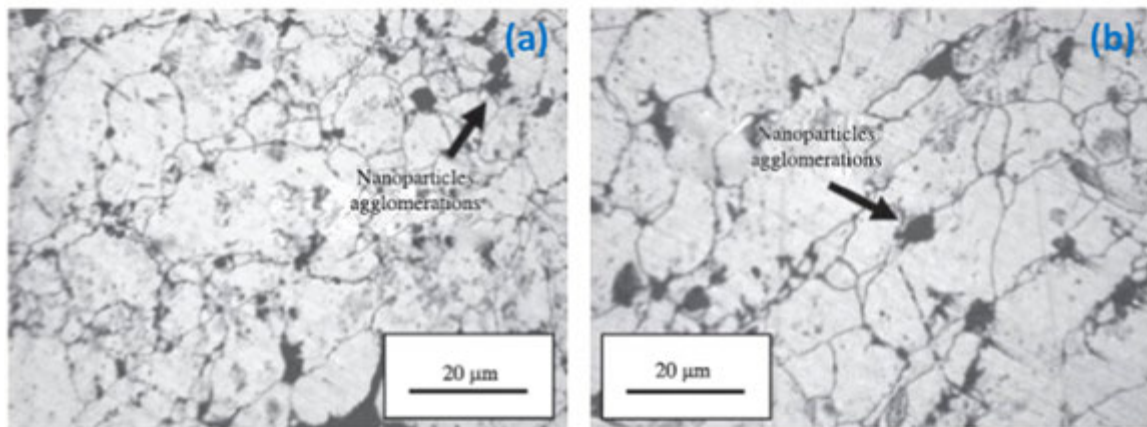


Fig. 7 Optical micrographs of (a) Al-5 vol% Al₂O₃ and (b) Al-5 vol% SiC nanocomposites. Reproduced from Mahmoud, T.S., *et al.*, 2012. Corrosion behaviour of Al/SiC and Al/Al₂O₃ nanocomposites. *Materials Research* 15 (6), 903–910.

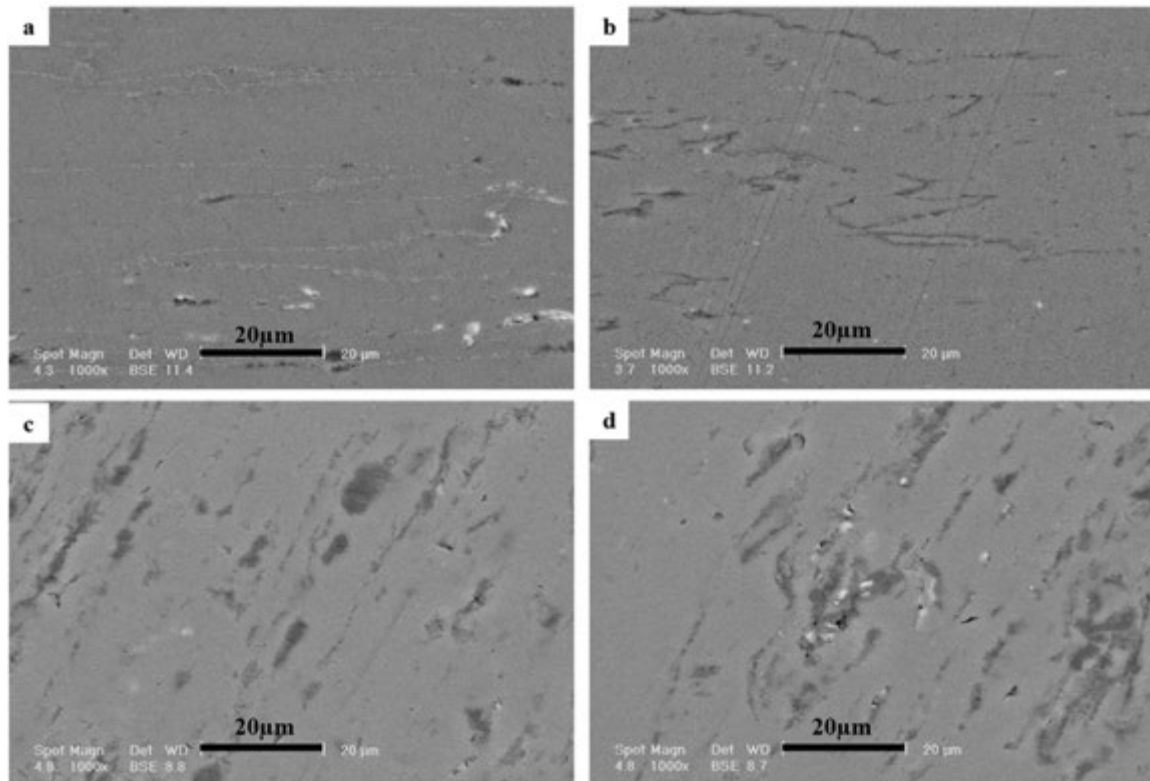


Fig. 8 SEM micrograph of extruded (a) pure Al and (b)–(d) Al-SiO₂ nanocomposites. Reproduced from Issa, H.K., *et al.*, 2017. Development of an aluminum/amorphous nano-SiO₂ composite using powder metallurgy and hot extrusion processes. *Ceramics International* 43 (17), 14582–14592.

superior wettability between matrix and reinforcement. The composites exhibited superior tensile strength with the addition of SiC owing to superior grain boundary strengthening. Hence, they claimed their method to be one of the most economical and efficient to produce Al-SiC nanocomposites.

Various mechanical properties of Al based nanocomposites improved, including the microhardness, tensile strength, depending upon the choice of reinforcement (type, particle size, and content) in the matrix. [Table 1](#) summarizes mechanical response of a number of aluminum based nanocomposite systems prepared using different processing methodologies. It was observed that microhardness, yield strength, and tensile strength tend to increase, and ductility decreases with the increasing volume fraction of nanosized particulates. Tensile properties such as yield strength and tensile strength generally tend to improve with decreasing particle size for a given volume fraction of reinforcement.

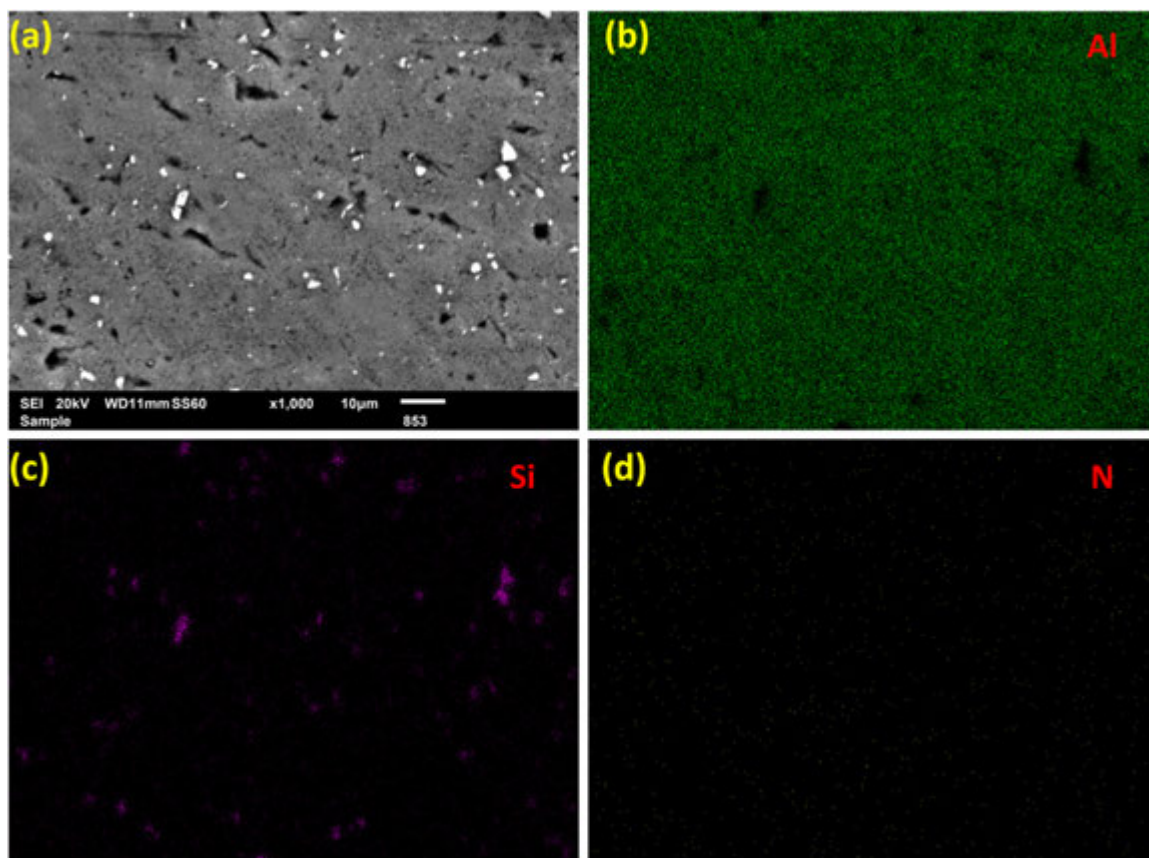


Fig. 9 (a) SEM micrograph of extruded Al-1.5 vol% Si₃N₄ nanocomposite and corresponding EDS mapping images of (b) Al, (c) Si, and (d) N elements. Reproduced from Matli, P.R., *et al.*, 2017b. Improved properties of Al-Si₃N₄ nanocomposites fabricated through a microwave sintering and hot extrusion process. RSC Advances 7 (55), 34401–34410.

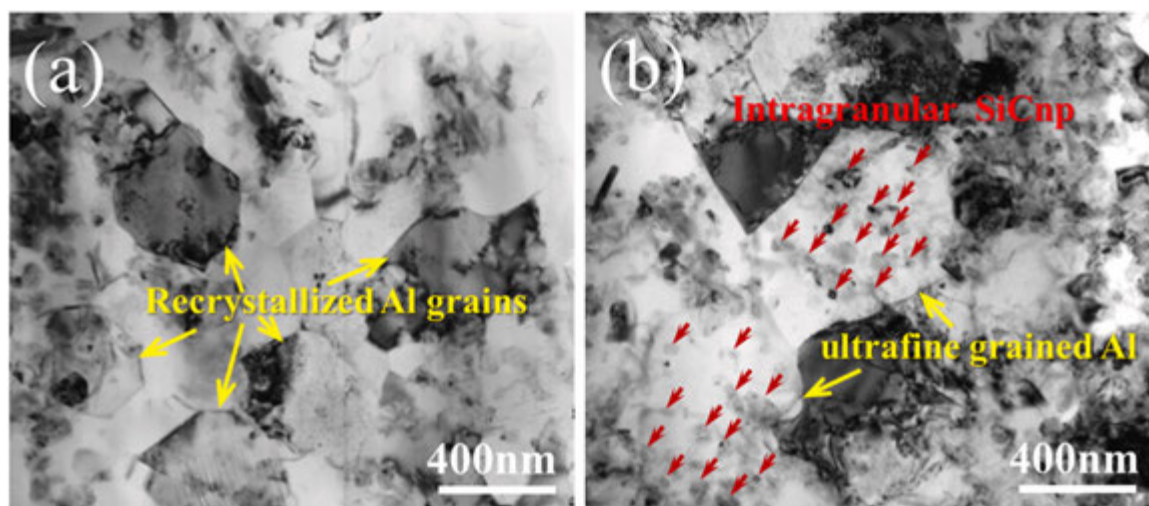


Fig. 10 Bright field TEM micrographs of the extruded 10 vol% SiC/Al nanocomposites. Reproduced from Li, A., *et al.*, 2019. Enhanced combination of strength and ductility in ultrafine-grained aluminum composites reinforced with high content intragranular nanoparticles. Materials Science and Engineering: A 745, 10–19.

Table 1 Hardness and tensile properties of Al-based nanocomposites

Materials	Synthesis route	Particle size	Hardness (Hv)	Tensile properties		
				0.2% TYS (MPa)	UTS (MPa)	Ductility (%)
Pure Al	Microwave sintering + Hot extrusion (Matli <i>et al.</i> , 2017b)	15–30 nm	37 ± 3	105 ± 2	116 ± 4	13.6 ± 0.3
Al – 0.5 vol% Si ₃ N ₄			58 ± 4	124 ± 4	139 ± 7	11.2 ± 0.3
Al – 1.0 vol% Si ₃ N ₄			72 ± 3	140 ± 5	163 ± 5	9.3 ± 0.5
Al – 1.5 vol% Si ₃ N ₄			101 ± 5	165 ± 8	191 ± 6	7.2 ± 0.4
Al–0.3 vol% SiC	Microwave sintering + Hot extrusion (Reddy <i>et al.</i> , 2017)	15 nm	49 ± 6	117 ± 2	130 ± 3	11.9 ± 1.3
Al–0.5 vol% SiC			56 ± 3	125 ± 3	144 ± 7	9.8 ± 0.8
Al–1.0 vol% SiC			73 ± 4	140 ± 5	160 ± 9	8.6 ± 0.6
Al–1.5 vol% SiC			82 ± 4	158 ± 9	178 ± 6	7.3 ± 0.9
Al – 0.5 vol% TiC	Microwave sintering + Hot extrusion (Reddy <i>et al.</i> , 2018a)	50 nm	46 ± 3	117 ± 5	135 ± 4	10.2 ± 0.3
Al – 1.0 vol% TiC			79 ± 5	128 ± 3	151 ± 6	8.1 ± 0.2
Al – 1.5 vol% TiC			94 ± 6	151 ± 2	186 ± 3	7.2 ± 0.3
Al – 0.5 vol% B ₄ C	MWS + Hot extrusion (Ubaid <i>et al.</i> , 2017)	10 nm	78.85	132.68	156.9	10.6
Al – 1.0 vol% B ₄ C			135.56	173.14	194.41	7.7
Pure Al	Powder metallurgy + hot extrusion (Issa <i>et al.</i> , 2017)	30–50 nm	27.6	78	119	0.28
Al – 1 wt% SiO ₂			39.15	85	148.5	0.26
Al – 2 wt% SiO ₂			38.7	95	142.77	0.12
Al – 3 wt% SiO ₂			38.7	100	136.68	0.09
Al – 0.5 vol% BN	Microwave sintering + hot extrusion (Reddy <i>et al.</i> , 2018b)	30–50 nm	48 ± 4	119 ± 6	127 ± 3	10.4 ± 0.2
Al – 1.0 vol% BN			67 ± 3	126 ± 3	137 ± 6	8.2 ± 0.5
Al – 1.5 vol% BN			88 ± 4	144 ± 2	158 ± 4	6.9 ± 0.4
Pure Al	Stir casting technique (Pradhan <i>et al.</i> , 2016)	–	56 ± 2	62.6	123.1	–
Al-Fe aluminides			79 ± 4	95.8	197.5	–
Pure Al	Ultrasound assisted stirring (Ma <i>et al.</i> , 2017)	–	40.2	111	127	13.5
Al – 1 wt% SiC			50.4	132	157	8.8
Al – 2 wt% SiC			53.8	135	163	5.9
Al – 3 wt% SiC			56.1	142	162	4.7
Pure Al	SPS + hot extrusion (Zeng <i>et al.</i> , 2018)	20 nm	22	52	85	0.17
Al – 5 vol% CNT			52	105	194	0.11
Pure Al	Accumulative Roll Bonding (ARB) (Ramkumar and Natarajan, 2019)	30 nm	44	–	52	–
Al – 0.75 wt% TiO ₂			65	–	96	–
Al – 1.5 wt% TiO ₂			83	–	163	–
Al – 2.25 wt% TiO ₂			97	–	210	–
Al – 3 wt% TiO ₂			116	–	265	–
Pure Al	Spark plasma sintering (Bisht <i>et al.</i> , 2017)	6–8 nm	–	55	68	2.6
Al – 0.5 wt% GNP			–	51	80	1.6
Al – 1 wt% GNP			–	66	103	1.4
Al – 3 wt% GNP			–	37	44	0.5
Al – 5 wt% GNP			–	22	27	0.02

Matli *et al.* (2017a) used the powder metallurgy technique to fabricate Al-SiC, Al-Si₃N₄, and Al-Al₂O₃ composites. An example of the enhancement in microhardness in the case of microwave-assisted hot extruded Al-SiC, Al-Si₃N₄, and Al-Al₂O₃ composites can be seen in Fig. 11. The experimental results also showed that the highest hardness was obtained for 15-nm Si₃N₄ reinforced aluminum nanocomposites when compared to 35-nm (SiC) reinforced aluminum illustrating also the effect of size of nanoreinforcement.

Isa *et al.* studied the tensile properties of amorphous nano SiO_2/Al composites prepared by powder metallurgy and extrusion. Results showed that with the addition of 1 wt% amorphous silica nanoparticle to Al, the tensile strength and hardness increased by about 24.8% and 41.8%, respectively (Issa *et al.*, 2017).

The influence of BN nanoparticles (0.5, 1.5, 3, 4.5, 6, and 7.5 wt%) content on the tensile strength of Al-BN nanocomposites was investigated by Pradhan *et al.* (2016). It was observed that the addition of 4.5 wt% BNNP reinforcements to aluminum matrix leads to an $\sim 50\%$ improvement in tensile strength when compared to unreinforced aluminum. Further, the composites with 4.5 wt% BNNP showed 190% higher yield stress than that of pure aluminum when it was tested at 300°C .

Reddy *et al.* (2017) studied the room temperature tensile properties of SiC reinforced aluminum matrix nanocomposites. Silicon carbide particles with an average particle size of ~ 15 nm were used in the study. The best combination of yield and tensile strengths was observed in the case of Al-1.5 vol% SiC, which are $\sim 51\%$ and $\sim 49\%$ greater than the pure Al. The microwave-hot extruded Al-SiC nanocomposites showed considerable improvement in hardness and tensile strength in comparison with the stir cast processed materials (Table 1).

Reddy *et al.* (2018a), in another study, reinforced TiC particles (50 nm) to pure aluminum using microwave sintering and hot extrusion to improve their mechanical properties. The obtained room temperature tensile engineering stress-strain relationship of the developed Al and Al-TiC are presented in Fig. 12. The results indicated that the incorporation of 1.5 vol% of TiC nanoparticles to Al led to an increase of 41% in Young's modulus, and 56.3% in UTS, while ductility decreased by $\sim 42\%$.

Karbalaee Akbari *et al.* (2013) used a novel approach to fabricate A356-based nanocomposites containing Al_2O_3 nanoparticles. The Al_2O_3 nanoparticles were ball milled for 1, 4, 8, 16, and 24 h. Stir casting method was used for processing the

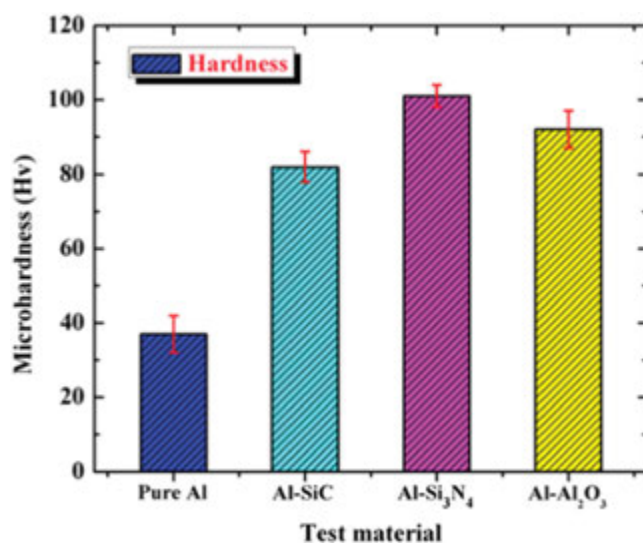


Fig. 11 Hardness of aluminum metal matrix composites. Reproduced from Matli, P.R., *et al.*, 2017a. Development of metal matrix composites using microwave sintering technique. In: Sintering of Functional Materials. IntechOpen.

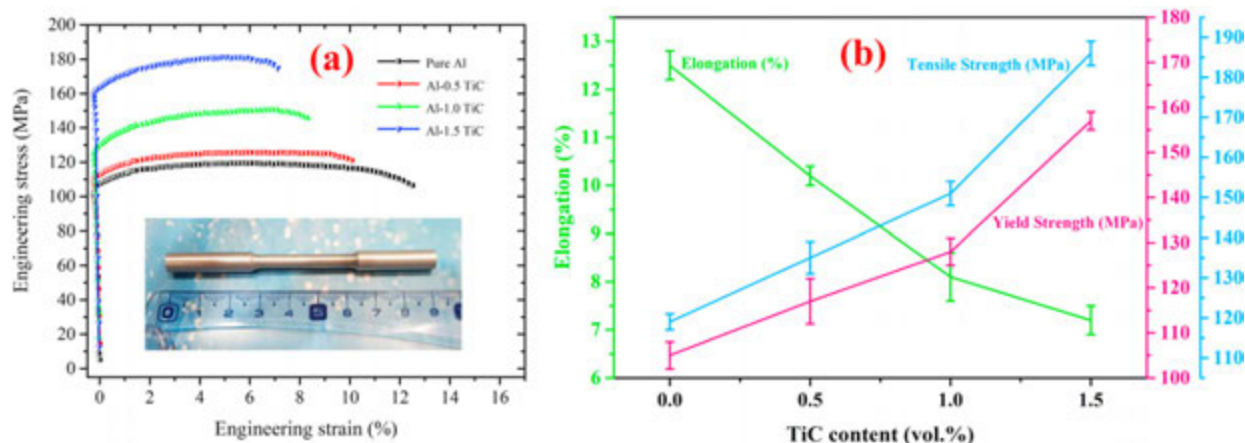


Fig. 12 (a) Tensile stress-strain curves of the Al-TiC nanocomposites and (b) variations of elongation, strength (yield & tensile) of the composites with different amounts of TiC. Reproduced from Reddy, M.P., *et al.*, 2018a. Enhancing thermal and mechanical response of aluminum using nanolength scale TiC ceramic reinforcement. *Ceramics International* 44 (8), 9247–9254.

nanocomposites. A considerably uniform distribution of Al_2O_3 nanoparticles was observed in the composites. However, the tensile strength and hardness of the nanocomposites decreased with an increase in ball milling time of Al_2O_3 nanoparticles.

Steinman *et al.* (2018) studied the microstructure and interface characteristics of BN, AlB_2 , and AlN particles (0, 1, 3, 5, and 7 wt%) containing aluminum matrix nanocomposites. These nanocomposites were fabricated via ball milling followed by novel spark plasma sintering. The room and elevated (500°C) temperature tensile tests results showed an increase in the case of Al-BN composites with the progressive addition of the secondary BN phase. The maximum strength of 170 MPa was observed for the Al-BN composite. The Al- AlB_2 sample showed a value of 80 MPa, which is still 60% higher than that of Al, whereas the Al-AlN samples exhibited 30 MPa strength which is lower than that of pure Al (42 MPa).

Pradhan *et al.* (2016) studied the Fe-aluminide particles reinforced Al composites produced by stir casting method. Microstructural characterization of Al-Fe aluminide composites revealed the formation of intermetallic phase $\text{Al}_{13}\text{Fe}_4$. The incorporation of Fe-aluminides particles into pure Al matrix resulted in the progressive improvement of ultimate tensile strength and 0.2% yield strength values in all composites. The mechanical properties of the Al-Fe aluminide composites are shown in Table 1.

Kwon *et al.* (2009) reported the synthesis and mechanical properties of aluminum/carbon nanotube (CNT) composites using spark plasma sintering (SPS) followed by hot extrusion. The distribution of carbon nanotubes in the matrix was improved by the superior wettability between reinforcement and aluminum. Results of microhardness measurements revealed that increasing the volume fraction of CNTs leads to an increase in the hardness of aluminum nanocomposites. It was reported that the slight addition of 5 vol% CNTs to aluminum leads to a 200% improvement in the ultimate tensile strength (194 MPa) compared to pure aluminum. The combination of SPS and hot extrusion method exhibit a good level of mechanical properties with carbon nanotube. However, this technique is expensive and has its processing limitations.

Bisht *et al.* (2017) synthesized Al-GNP nanocomposite with GNP average particle size and thickness of 15 μm and 6–8 nm, respectively. The composites were synthesized by spark plasma sintering technique. Effect of different amount of GNPs was evaluated. XRD analysis, scanning/transmission electron microscopy confirmed the presence of graphene particles in the aluminum matrix. The hardness increased by 21.4%, yield strength and ultimate tensile strength increased by 84.5% and 54.8%, respectively, by adding only 1.0 wt% of graphene nanoplatelets (GNPs) to the matrix (Fig. 13).

The effect of nano Al_2O_3 particles on the mechanical and microstructure properties of the Al- Al_2O_3 nanocomposites was investigated by Ramkumar and Natarajan (2019). They reported that the yield strength and tensile strength of 5 wt% Al_2O_3 /Al nanocomposite showed an increase of about ~23% and 26%, respectively, when compared to the Al matrix.

SEM micrograph of fracture surfaces of failed tensile pure aluminum and Al-1.5 vol% TiC nanocomposite samples are shown in Fig. 14. The center part of fracture surfaces exhibited predominantly ductile failure which contained fine dimples, while the lips contained oval dimples and sheared faces. Fig. 14(b) shows a small and large dimples. Large dimples were found to contain clusters of TiC nanoparticles.

Future Work

The results presented in the previous sections indicate that substantial research has been conducted to develop aluminum based nanocomposites. However, there is still a large area for improvements which could be topics for further research and development activities on aluminum-based nanocomposites. Very few investigations are made on the understanding of the strengthening effect of nanometric particulates, response to different loading conditions, as well as to determine the influence of strain rates and temperature to develop high-performance nanocomposites. Further, HRTEM and electron diffraction studies are required to confirm the presence/absence of secondary in-situ reactions due to the presence of secondary phases and reinforcements in different types of processing methods. In addition, other kinds of nanometric reinforcements such as reduced graphene oxide (rGO) with different sizes and shapes can be incorporated into the Al-matrix to develop new Al-based nanocomposites. Aluminum/(ceramic + metal) hybrid nanocomposites with different combinations of ceramic + metal hybrid reinforcements can additionally be explored to simultaneously improve the strength and ductility properties.

Summary

The present article reviews the recent advancements in the microstructural and tensile response of the aluminum-based nanocomposites containing different types of nano ceramic reinforcements processed using various synthesis techniques. The following conclusions can be drawn from this work.

- Al-based nanocomposites have great potential due to their superior overall performance. These composites are foreseen to have considerable applications in weight-critical automobiles, sports, aerospace, electronics sectors.
- Literature review clearly validates that nanoparticles reinforced aluminum composites can be prepared using different routes such as powder metallurgy, squeeze casting, spark plasma sintering, etc. However, the powder metallurgy assisted microwave sintering route is one of the most promising routes in the context of cost, time and energy savings.
- Mechanical properties including hardness and tensile properties of the Al-based nanocomposites synthesized using powder metallurgy-microwave sintering-hot extrusion process are superior compared to other synthesis routes like casting, ultrasound-assisted stirring, and spark plasma sintering.

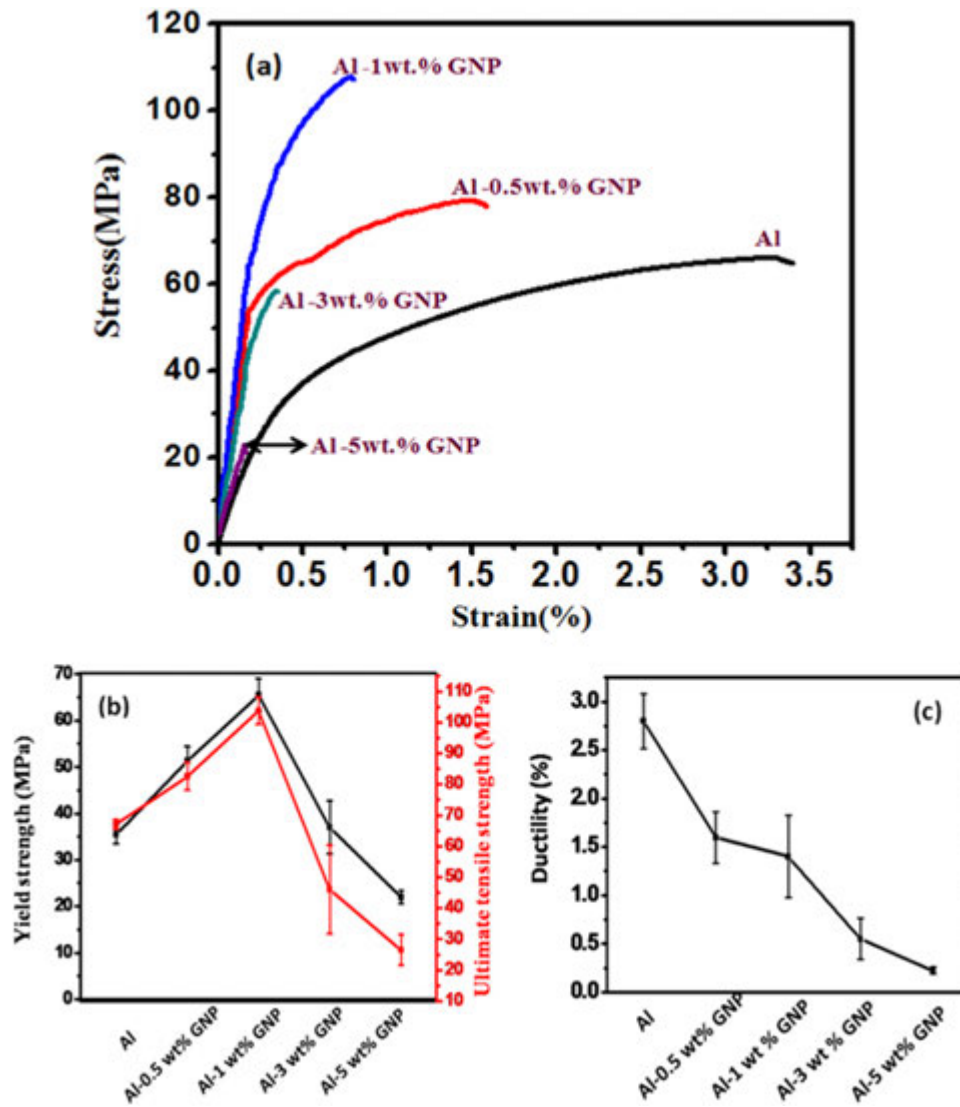


Fig. 13 (a) Stress–strain curve; variation of (b) yield and ultimate tensile strength and (c) ductility for Al and Al-GNP nanocomposites. Reproduced from Bisht, A., *et al.*, 2017. Strengthening mechanism in graphene nanoplatelets reinforced aluminum composite fabricated through spark plasma sintering. *Materials Science and Engineering: A* 695, 20–28.

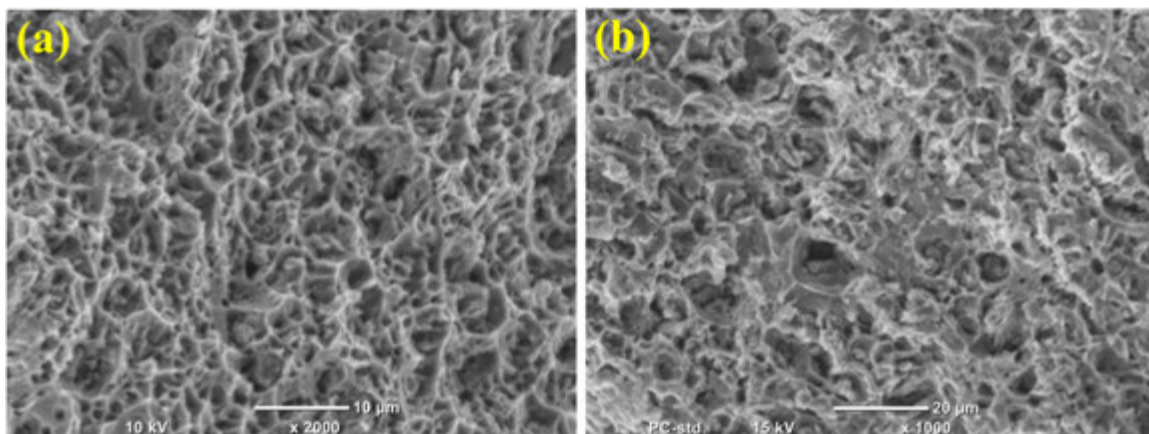


Fig. 14 SEM fractography of (a) Pure Al and (b) Al-1.5 vol% TiC under tensile loading. Reproduced from Reddy, M.P., *et al.*, 2018a. Enhancing thermal and mechanical response of aluminum using nanolength scale TiC ceramic reinforcement. *Ceramics International* 44 (8), 9247–9254.

References

- Abbass, M.K., Fouad, M.J., 2014. Study of wear behavior of aluminum alloy matrix nanocomposites fabricated by powder technology. *Engineering and Technology Journal* 32, 1720–1732.
- Babalola, P., *et al.*, 2014. Development of aluminium matrix composites: A review. *Online International Journal of Engineering and Technology Research* 2, 1–11.
- Bisht, A., *et al.*, 2017. Strengthening mechanism in graphene nanoplatelets reinforced aluminum composite fabricated through spark plasma sintering. *Materials Science and Engineering: A* 695, 20–28.
- Chawla, N., Chawla, K., 2006. Metal-matrix composites in ground transportation. *JoM* 58 (11), 67–70.
- Clyne, T., Withers, P., 1995. *An Introduction to Metal Matrix Composites*. Cambridge University Press.
- El-Kady, O., Fathy, A., 2014. Effect of SiC particle size on the physical and mechanical properties of extruded Al matrix nanocomposites. *Materials & Design* 54, 348–353.
- El-Labban, H.F., *et al.*, 2014. Coating of 6028 aluminum alloy using aluminum piston alloy and Al-Si alloy-based nanocomposites produced by the addition of Al-Ti5-B1 to the matrix melt. *Metallurgical and Materials Transactions B* 45 (5), 1608–1614.
- Fogagnolo, J., *et al.*, 2003. Effect of mechanical alloying on the morphology, microstructure and properties of aluminium matrix composite powders. *Materials Science and Engineering: A* 342 (1–2), 131–143.
- Ibrahim, I., *et al.*, 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science* 26 (5), 1137–1156.
- Ipek, R., 2005. Adhesive wear behaviour of B₄C and SiC reinforced 4147 Al matrix composites (Al/B₄C–Al/SiC). *Journal of Materials Processing Technology* 162, 71–75.
- Issa, H.K., 2017. Development of an aluminum/amorphous nano-SiO₂ composite using powder metallurgy and hot extrusion processes. *Ceramics International* 43 (17), 14582–14592.
- Kang, Y.-C., Chan, S.L.-I., 2004. Tensile properties of nanometric Al₂O₃ particulate-reinforced aluminum matrix composites. *Materials Chemistry and Physics* 85 (2–3), 438–443.
- Karbalaee Akbari, M., *et al.*, 2013. Fabrication of nano-sized Al₂O₃ reinforced casting aluminum composite focusing on preparation process of reinforcement powders and evaluation of its properties. *Composites Part B: Engineering* 55, 426–432.
- Kwon, H., *et al.*, 2009. Combination of hot extrusion and spark plasma sintering for producing carbon nanotube reinforced aluminum matrix composites. *Carbon* 47 (3), 570–577.
- Li, A., *et al.*, 2019. Enhanced combination of strength and ductility in ultrafine-grained aluminum composites reinforced with high content intragranular nanoparticles. *Materials Science and Engineering: A* 745, 10–19.
- Lloyd, D., 1994. Particle reinforced aluminium and magnesium matrix composites. *International Materials Reviews* 39 (1), 1–23.
- Ma, P., *et al.*, 2017. Effect of Al₂O₃ Nanoparticles as Reinforcement on the Tensile Behavior of Al-12Si Composites. *Metals* 7 (9), 359.
- Ma, Z., *et al.*, 1996. Nanometric Si₃N₄ particulate-reinforced aluminum composite. *Materials Science and Engineering: A* 219 (1–2), 229–231.
- Mahmoud, T.S., *et al.*, 2012. Corrosion behaviour of Al/SiC and Al/Al₂O₃ nanocomposites. *Materials Research* 15 (6), 903–910.
- Mathew, J., *et al.*, 2018. Potential applications of nanotechnology in transportation: A review. *Journal of King Saud University-Science* 31, 586–594.
- Matli, P., *et al.*, 2016. Microwave rapid sintering of Al-metal matrix composites: A review on the effect of reinforcements, microstructure and mechanical properties. *Metals* 6 (7), 143.
- Matli, P.R., *et al.*, 2017a. Development of metal matrix composites using microwave sintering technique. In *Sintering of Functional Materials*. IntechOpen.
- Matli, P.R., *et al.*, 2017b. Improved properties of Al–Si₃N₄ nanocomposites fabricated through a microwave sintering and hot extrusion process. *RSC Advances* 7 (55), 34401–34410.
- Miracle, D., 2005. Metal matrix composites – From science to technological significance. *Composites Science and Technology* 65 (15–16), 2526–2540.
- Prabhu, B., *et al.*, 2006. Synthesis and characterization of high volume fraction Al–Al₂O₃ nanocomposite powders by high-energy milling. *Materials Science and Engineering: A* 425 (1–2), 192–200.
- Pradhan, S., *et al.*, 2015. Wear characteristics of Al–AlN composites produced in-situ by nitrogenation. In: *Proceedings of the IOP Conference Series: Materials Science and Engineering*. IOP Publishing.
- Pradhan, S.K., *et al.*, 2016. A simple stir casting technique for the preparation of in situ Fe-aluminides reinforced Al-matrix composites. *Perspectives in Science* 8, 529–532.
- Ramkumar, K., Natarajan, S., 2019. Effects of TiO₂ nanoparticles on the microstructural evolution and mechanical properties on accumulative roll bonded Al nanocomposites. *Journal of Alloys and Compounds* 793, 526–532.
- Rawal, S.P., 2001. Metal-matrix composites for space applications. *JoM* 53 (4), 14–17.
- Reddy, M.P., *et al.*, 2018a. Enhancing thermal and mechanical response of aluminum using nanolength scale TiC ceramic reinforcement. *Ceramics International* 44 (8), 9247–9254.
- Reddy, M.P., *et al.*, 2018b. Enhancing compressive, tensile, thermal and damping response of pure Al using BN nanoparticles. *Journal of Alloys and Compounds* 762, 398–408.
- Reddy, M.P., *et al.*, 2017. Enhanced performance of nano-sized SiC reinforced Al metal matrix nanocomposites synthesized through microwave sintering and hot extrusion techniques. *Progress in Natural Science: Materials International* 27 (5), 606–614.
- Rino, J.J., *et al.*, 2012. An overview on development of aluminium metal matrix composites with hybrid reinforcement. *International Journal of Science and Research* 1 (3), 34 (2), 163–170.
- Singh, V., *et al.*, 2015. Enhancement of wettability of aluminum based silicon carbide reinforced particulate metal matrix composite. *High Temperature Materials and Processes* 34 (2), 163–170.
- Steinman, A.E., *et al.*, 2018. Al-based composites reinforced with AlB₂, AlN and BN phases: Experimental and theoretical studies. *Materials & Design* 141, 88–98.
- Suresh, S., *et al.*, 1993. *Fundamentals of Metal Matrix Composites*. Heinemann.
- Toozandehjani, M., *et al.*, 2017. Effect of milling time on the microstructure, physical and mechanical properties of Al–Al₂O₃ nanocomposite synthesized by ball milling and powder metallurgy. *Materials* 10 (11), 1232.
- Topcu, I., *et al.*, 2009. Processing and mechanical properties of B₄C reinforced Al matrix composites. *Journal of Alloys and Compounds* 482 (1–2), 516–521.
- Ubaid, F., *et al.*, 2017. Using B₄C nanoparticles to enhance thermal and mechanical response of aluminum. *Materials* 10 (6), 621.
- Venci, A., Rac, A., 2004. New wear resistant Al based materials and their application in automotive industry. *MVM–International Journal for Vehicle Mechanics, Engines and Transportation System* 30, 115–139.
- Yang, J.H., *et al.*, 2004. Microwave process for sintering of uranium dioxide. *Journal of Nuclear Materials* 325 (2–3), 210–216.
- Zakaria, H., 2014. Microstructural and corrosion behavior of Al/SiC metal matrix composites. *Ain Shams Engineering Journal* 5 (3), 831–838.
- Zeng, X., *et al.*, 2018. Microstructure and mechanical properties of Al–SiC nanocomposites synthesized by surface-modified aluminium powder. *Metals* 8 (4), 253.

Compressive Response of Aluminum Metal Matrix Composites

Ramanathan Arunachalam, Sultan Qaboos University, Muscat, Oman

Pradeep K Krishnan, National University of Science and Technology, Muscat, Oman

© 2021 Elsevier Inc. All rights reserved.

Nomenclature

Al	Aluminum	SEM	Scanning electron microscope
Al ₂ O ₃	Aluminum oxide	SGC	Stir gravity casting
AMMCs	Aluminum metal matrix composites	SiC	Silicon carbide
ARB	Accumulative roll bonding	Si ₃ N ₄	Silicon nitride
BN	Boron nitride	SiO ₂	Silicon dioxide
CNT	Carbon nanotube	SPS	Spark plasma sintering
CS	Centrifugal casting	TiB ₂	Titanium diboride
GPI	Gas pressure infiltration	TiC	Titanium carbide
HEBMMS	High energy ball milling and sintering	TiN	Titanium nitride
HPCI	High-pressure centrifugal infiltration	TiO ₂	Titanium dioxide
MI	Melt infiltration	Ti ₃ SiC ₂	Titanium silicon carbide
MMCs	Metal matrix composites	UCS	Ultimate compressive strength
MS	Microwave sintering	VGS	Vacuum gas sintering
MWCNT	Multi-wall carbon nanotube	VPI	Vacuum pressure infiltration
PI	Pressure infiltration	WS ₂	Tungsten disulfide
SC	Stir casting	ZnO	Zinc oxide
SD	Spray deposition	ZrB ₂	Zirconium diboride
SE	Screw extrusion	ZrO ₂	Zirconium dioxide

Glossary

Alloy A substance that has metallic properties comprising of two or more chemical compounds, at least one of which is a metal.

Casting A process whereby hot liquid metal flows into a mold and solidifies in the mold cavity shape.

Cavitation The formation of space within a solid object or body.

Cohesion The force with which like particles are bound together.

Composite A combination of two or more insoluble materials in each other, which exhibit superior properties to either of the component materials.

Corrosion resistance The ability of a material to resist damage due to oxidation or other chemical reactions caused by corrosion.

Crucible A ceramic pot made of reasonably high thermal conductivity materials such as graphite, bonded with clay or carbon, and used for melting metals.

Debonding It occurs when a reinforcement particle stops adhering to the substrate material (matrix).

Dendrite A crystal with branched appearances formed during the solidification of alloys.

Dispersion Distribution of secondary phase like reinforcement particles in a continuous phase like matrix material.

In-situ The reinforcement is formed within the matrix by reaction during the processing.

Metal matrix Acts as a continuous phase and accommodates the reinforcement material.

Nucleation The process that arises in the development of a crystal from a solution that arranges a small number of atoms, ions, or molecules in a pattern typical of a crystalline solid, creating a site where new particles are deposited as the crystal grows.

Reinforcement Material that enhances the strength or other mechanical properties of the composite.

Introduction

Wrought alloys of aluminum are usually linked to ductility, stiffness, higher strength, excellent resistance to corrosion, and excellent electrical conductivity (Stjohn and Nie, 2017). Cast alloys have appealing characteristics such as low melting point, high fluidity, stiffness, excellent corrosion resistance (Okayasu *et al.*, 2013), and superior as-solidified strength. Cast alloys are commonly used as castings of sand and die-castings. Casting alloys used in the most significant quantities contain silicon additions of 9.0%–13.0% far exceeding the amounts in most wrought alloys. Silicon is the alloying component, which makes the high-volume aluminum casting industry's business viability possible. Silicon content from 4.0% to 12.0% eutectic level reduces scrap losses, allows the manufacturing of much more complex models with higher section thickness differences, and yield castings with better

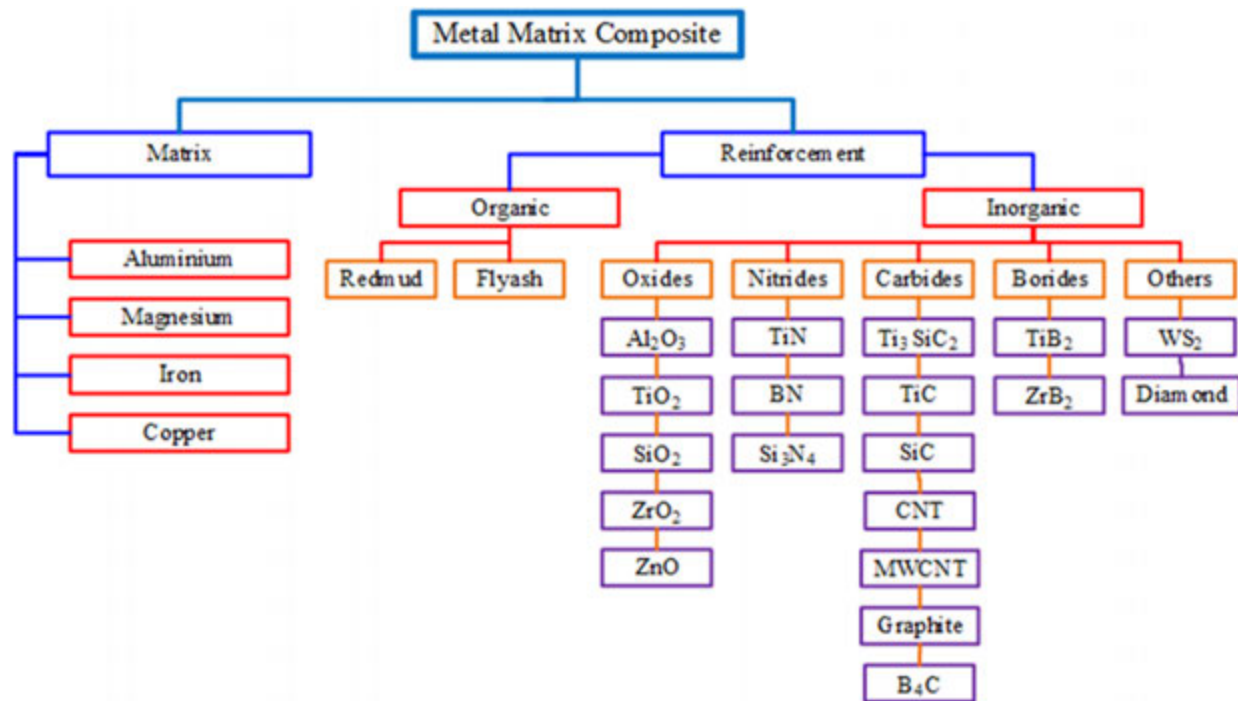


Fig. 1 Various matrix and reinforcement materials used for the production of MMCs. Reproduced from Arunachalam, R., Kumar, P., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *J. Manuf. Process.* 42, 213–245.

performance. These advantages stem from the impacts of silicon in growing fluidity, decreasing cracking, and improving feeding to minimize porosity during shrinkage. Their high resistance to corrosion makes these alloys beneficial for marine, aerospace, and automotive construction (Okayasu *et al.*, 2013). These cast alloys are used in the production of metal matrix composites (MMC). MMCs are metals that are reinforced with other metals, ceramics, or organic compounds (Ramnath *et al.*, 2014). MMCs are produced by dispersing some weight or volume percentage of reinforcements in the matrix materials. Various metals are available as matrix materials for the production of MMCs; some are Al, Mg, Cu, Fe, and Ti. Aluminum and its alloys are commonly used in the production of MMCs, among others. Due to its excellent thermal, mechanical properties, high strength to weight ratio, and superior corrosion resistance, AMMCs are potential materials for various applications. In the automotive industry, AMMCs find many applications, such as pistons, cylinder liners, brake rotors, driveshafts, and others.

Fig. 1 displays the various matrix and reinforcement materials that can be used to produce MMCs. The numerous inorganic reinforcements such as oxides (aluminum oxide, titanium oxides, zirconium oxides), carbides (silicon carbide, titanium carbide), nitrides (titanium nitride), borides (titanium boride, zirconium boride) are commonly used but are fairly expensive. Organic reinforcements such as fly ash and red mud significantly improve the strength of the composite, and its cost is relatively low.

The reinforcements could be particulates, fibers, or laminates. The reinforced composite using particulates plays the leading role in the manufacture of AMMCs, as they are readily available, inexpensive, and easier to disperse in the matrix. Among the various micro to nanosize reinforcement particles, SiC, B₄C, Al₂O₃ are the most widely used reinforced particles. These reinforcement particles improve the hardness and elastic modulus but enhance the wear resistance (Huang *et al.*, 2019). Due to its high hardness, specific strength, stiffness, and thermal properties, SiC is added while Al₂O₃ exhibits strong compressive strength and wear resistance. Boron carbide is one of the toughest known elements and has high elastic modulus and toughness to fracture (Arunachalam *et al.*, 2019).

The primary production processes for the manufacturing of aluminum MMCs can be classified according to the state in which they are shaped: Liquid state and solid state processes (Nturanabo *et al.*, 2019). The liquid state processes are further classified into liquid metal infiltration and liquid metal casting processes, as illustrated in **Fig. 2**. Specifically, liquid metal casting processes are the primary route for producing MMCs. The infiltration of liquid metal from such matrix alloys into a wide range of ceramic, boron, and carbon reinforcements had been a popular route for the production of such MMCs (Lim and Clegg, 1997). The production processes have a substantial impact on both the mechanical properties and production costs. **Fig. 2** also shows other methods (semi-solid and others, including in situ) used in the production of MMCs.

Within the liquid processing route, stir-squeeze casting is more widely used due to its simplicity and versatility. The stir-squeeze cast is a combination of casting (like in hydraulic forging) and squeezing. In this method, the solid material is heated above its melting point. Then the liquid metal is stirred with a stirrer creating a vortex into which the reinforcement material is added. The vortex created helps to produce a homogeneous mixture, and then the mixture is poured into a preheated die and subsequently

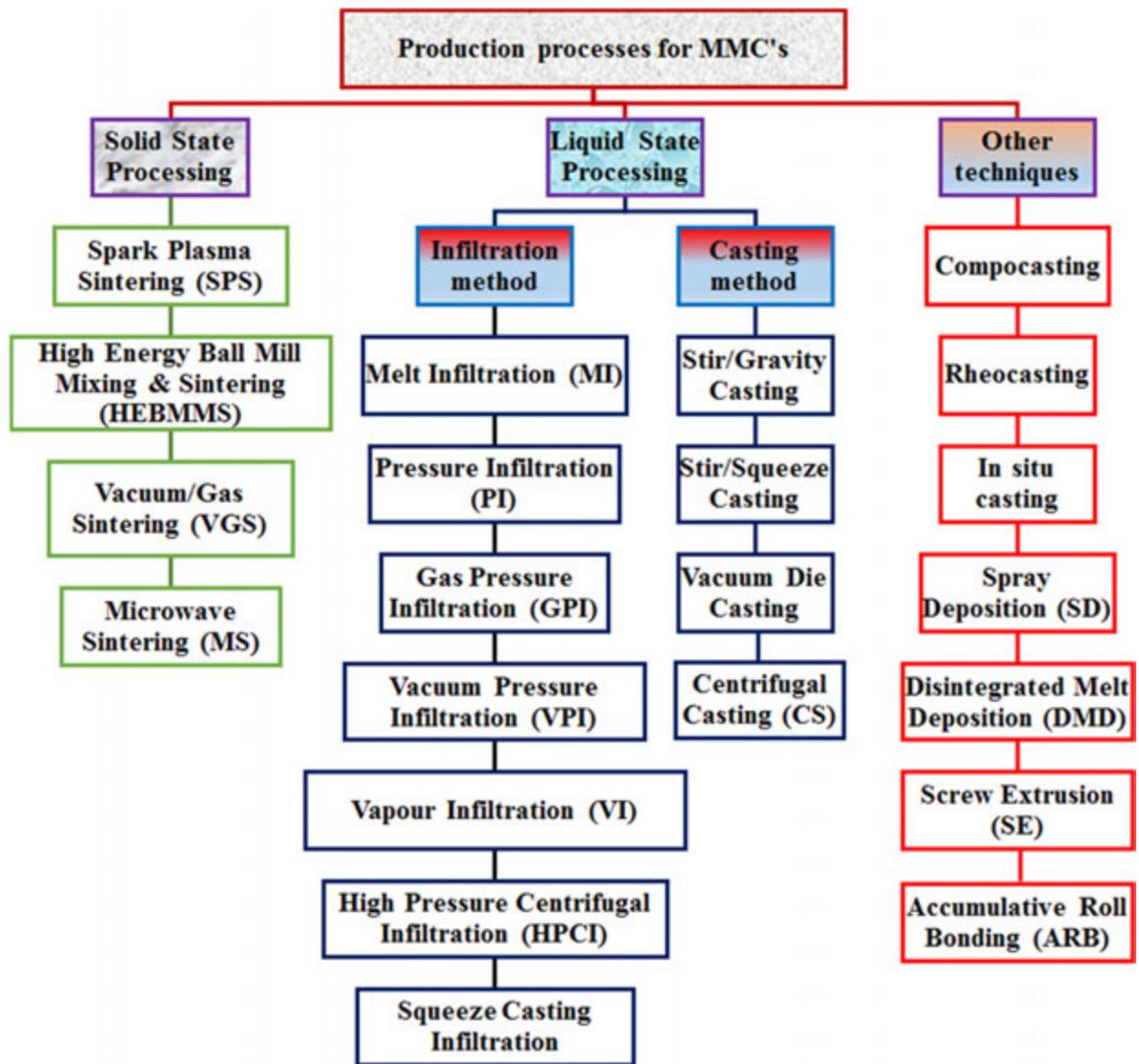


Fig. 2 The various production process for MMCs. Reproduced from Arunachalam, R., Kumar, P., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *J. Manuf. Process.* 42, 213–245.

hardened under the influence of a relatively high external pressure, using a hydraulic press. A hot runway pipe from the furnace to the die conveys the molten metal. The key advantages of this process are mass production flexibility, improved wettability between reinforcement and matrix material, and excellent mechanical properties due to the relatively high-pressure solidification (Panwar and Chauhan, 2018).

The suggested range of process parameters for stir-squeeze casting is given in Fig. 3. Among these parameters, squeeze pressure is the most influential. Most previous researchers stated 100 MPa squeeze pressure is ideal for grain refining and lower porosity. No substantial impacts were noted after 100 MPa squeeze pressure (Dhanashekar and Senthil Kumar, 2014). In order to enhance the product characteristics, squeeze stress holding time is recognized as the most influential factor. Therefore, the holding period between 30 and 45 s was suggested, after which there was no impact on the heat dissipation rate (Senthil and Amirthagadeswaran, 2012). The recommended melt temperature for aluminum alloys and composites is 700°C for the squeeze casting method. As the melt temperature decreased from 780 to 680°C, the microstructure gradually became finer, and the grains became smaller (Maleki et al., 2006). The temperature of the melt should be above 700°C for adequate infiltration of reinforcement (Yong and Clegg, 2005). Aluminum alloy tensile strength and elongation were reported to be rapidly enhanced as the preheating temperature of the die was increased from 200 to 250°C, but no drastic changes were observed with temperatures between 250 and 300°C. If the die temperature is further increased to 350°C, the tensile strength and elongation suddenly decreased, and many rosette particles were

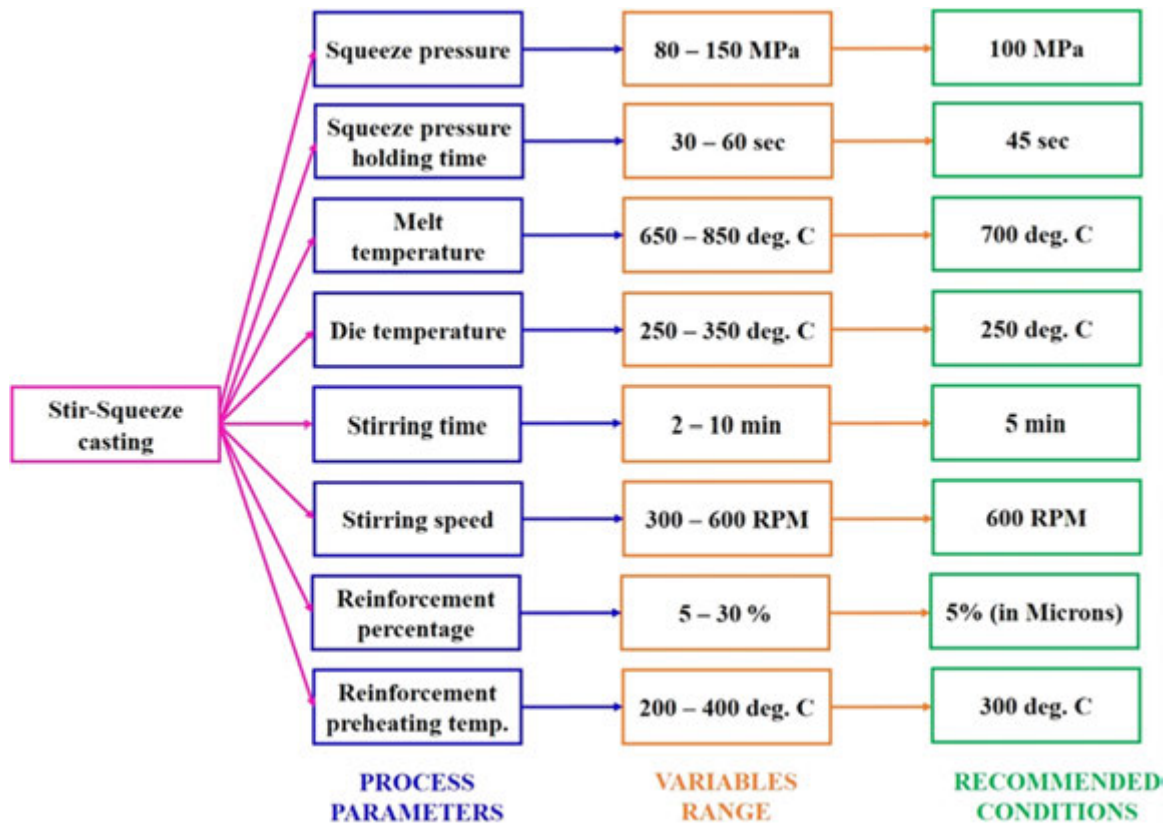


Fig. 3 Recommended process parameters for stir-squeeze casting process. Reproduced from Arunachalam, R., Kumar, P., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. J. Manuf. Process. 42, 213–245.

also observed in the microstructure (Dao *et al.*, 2012). To achieve a homogeneous mixture, the duration of the stirring time should be higher than 5 min and less than 10 min. The agglomeration of particles is observed over 10 min of stirring, thus reducing the mechanical properties of the composites (Umunakwe, 2017). The gas formation, oxide skin, and porosity were observed at higher stirring speeds (700 rpm) due to turbulence. At lower speeds, it was not appropriate to mix reinforcement with matrix, while the reinforcement was isolated from the vortex (Prabu *et al.*, 2006). The stirring speed of 600 rpm produces homogeneous mixture and less porosity in the MMCs, resulting in improved mechanical properties of the composites produced. The percentage of reinforcement purely depends on the desired properties of the AMMCs; for SiC and Al₂O₃ micro-sized particles, it was found to be 10% and 5%, respectively. For most reinforcement particles, preheating temperature of 250–300°C is suggested.

The focus of this article is on the mechanical properties, the mainly compressive strength of AMMCs produced through various production processes but primarily through the casting process. Based on the recent and relevant available literature, the mechanical properties, current applications, and the general strengthening mechanisms are discussed in the forthcoming sections.

Mechanical Properties of AMMCs

In compression testing, the sample or the component is compressed between two moving platens. A load cell and an extensometer or strain gauge are used to measure load and displacement. Compression tests are useful for testing material or component load-bearing capabilities under compressive loads. Compression pressure, for example, is taken into account in the design of tower structures, columns, bridge structures, and other load-bearing structures (Touchstone, 2020). The test is quite simple to conduct as well as the preparation of samples for testing. According to ASTM E9-09 (Reapproved 2018), solid cylindrical specimens of varying dimensions (short, medium, and long) can be used based on the availability of the sample materials (ASTM, 2010).

Material compression testing can be divided into two forms depending on the speed of the test: Static and dynamic modes. Static testing requires rates below 1 mm min⁻¹, while dynamic testing takes place at speeds > 10 mm min⁻¹. Static testing can be further categorized into axial and plane strain compression testing. The axial compression tests can provide the yield strength, ultimate strength, and modulus of materials that are used in the design of equipment structures and others. The plane strain compression test can be used in assessing the flow stress properties of materials, which is essential in selecting/sizing the

equipment in the manufacturing process such as rolling, forging, and extrusion. Besides, tests like flatwise compression testing are used in evaluating the collapse properties of laminates and composites (Touchstone, 2020).

AMMCs are potential materials for a wide variety of applications, such as aerospace, transportation, and defense due to their lightweight and excellent mechanical properties. Some of these applications, especially in aerospace and defense, the structural components are subjected to dynamic loadings such as bird hit or missile attack during their service life (Jo *et al.*, 2019). Compression load conditions are encountered in structural sections such as fuselage/pressure cabin lower skin, upper wing skin stringers, and lower horizontal stabilizers of a typical aircraft (Gloria, 2019). Compressive yield strength is the leading engineering property required for these aircraft applications. Not much literature reports the compressive response of AMMCs, and among the available literature on compression strength, most of them focus on the static mode, especially the axial-load compression testing and very few on the dynamic conditions.

Stir cast AMMCs are manufactured by adding reinforcement particles of different sizes ranging from micro to nano into the molten Al metal matrix. Most of the ceramic reinforcements do not have the wettability to be uniformly mixed in the matrix, and namely, wetting agents like magnesium (about 1 wt%) is added. Even with that, the reinforcements are not uniformly distributed, and other factors such as stirring speed, stirring time, stirrer blade configuration, and amount of reinforcement added significantly influence the distribution. Heterogeneous distribution of reinforcement particles has a negative influence on the mechanical properties such as compressive strength of MMC (Aktaş and Anil, 2018). Tables 1 and 2 summarize the mechanical properties of different AMMCs developed by researchers worldwide over the last ten years using micro and nano-sized reinforcing particles, respectively, through the stir casting route. The compressive strength impact of Al_2O_3 content is substantial. Thicker Al_2O_3 interface can result in stress localization, resulting in reduced mechanical characteristics (Tahamtan *et al.*, 2013). Thus, the compression strength of nanocomposites is higher than that of micro-composites because, in strengthening the composites, nano-particles are more efficient (Sajjadi *et al.*, 2012). The addition of 8% TiC particulates enhances the mechanical behavior of AA 7075 composites (Rao *et al.*, 2014). By increasing the weight percentage of microsize SiC particles, the compressive strength increases. The improvement in compressive strength can be attributed to the grain refinement and intense multidirectional thermal stress at the Al/SiC interface, which plays a significant role. SiC particles have a grain-refined strengthening effect, which is improved by increasing the weight percentage of SiC particles. The SiC particles function as the heterogeneous nucleation catalyst for aluminum during solidification (Rana *et al.*, 2015).

It is observed from Tables 1 and 2 that the particle size plays a critical role in improving the composite strength. The hardness and compressive strength are higher, and the porosity percentage is lower for the composites produced with nanosize particles as reinforcement.

Kumar *et al.* (2019) examined the feasibility of using scrap aluminum alloy wheels (SAAWs) from cars as matrix material and spent alumina catalyst (SAC) from oil refineries as reinforcing material, and compared the properties with LM25 as matrix and pure Al_2O_3 as reinforcement. To determine the compression characteristics and fracture patterns, the compression test was performed on four distinct samples. Fig. 4 displays the stress-strain curves obtained from the compression test carried out on the LM25 + Al_2O_3 composite. The LM25 + Al_2O_3 composite showed the highest compressive strength at deformation up to 8 mm from the initial height. In contrast, the LM25 + spent alumina catalyst composite showed the lowest compression strength value with a significant decrease in the composite's load-bearing capacity. The impact of the reinforcement type and its size on both the tensile strength and the compressive strength was substantial. LM25 + Al_2O_3 reinforced composites display improvement of 48% in the ultimate compressive strength relative to those reinforced with spent aluminum catalysts. This result demonstrates a significant impact of alumina mixed with a silicon eutectic phase on reinforcing composites by serving as a barrier to the propagation of cracks. The presence of a friction constraint between the flat sample contact ends resulted in the compressed samples having a non-uniform plastic flow. Such non-uniformity of flow and associated materials weakened the composites and caused shear deformation in the diagonal plane. The higher concentration of Al_2O_3 compared to the spent aluminum catalyst and the higher Si content in the LM25 matrix compared to the scrap aluminum alloy contributed to the creation of more nucleation sites for the mixture of alumina and eutectic silicon. The increase in the number of nucleation sites helps to achieve smaller grain sizes because of which the ultimate compressive strength is substantially higher in the two composites. The combination of acicular eutectic silicon and grain boundary reinforcement improved the mechanical characteristics. The intergranular distribution at the grain boundary provided better mechanical properties and prevented failure along the grain boundary. The smaller grain size of the LM25 matrix and the addition of Al_2O_3 led to enhanced mechanical characteristics. The smaller size of the aluminum reinforcement provided the eutectic silicon phase with additional nucleation sites (Kumar *et al.*, 2019).

Table 3 lists the latest applications of various AMMCs. It is very clear from this table that AMMCs have commercial significance, and so researchers can make use of it to advance the utilization of AMMCs. Table 3 could serve as a swift reference in selecting an AMMC for the mechanical properties/applications required.

Strengthening Mechanisms in AMMCs

Most of the engineering materials (metals and alloys) used in engineering are load-bearing materials. Hence, these materials must have adequate strength so as not to fracture during loading and also retain their strength (Bhat and Arunachalam, 1980). Strengthening of material is necessary because metals and alloys usually do not exhibit the desired strength due to the nature of metallic bonding and also because of a number of defects in the lattice. It is not recommended to change the crystal structure of the material or to change the nature of metallic bonding as it may lead to a brittle material. Strengthening of material should be

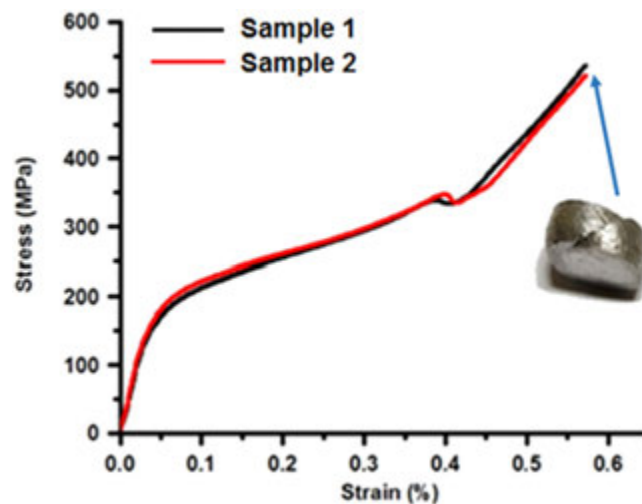
Table 1 Properties of AMMCs produced through stir casting process using microsize reinforcement

S. No.	Composites	Wt./ Vol. fraction (%)	Casting method	Particle size	Porosity (%)	Hardness	UCS (Mpa)	References
1	A356 (Al-Si7Mg)/Al ₂ O ₃	1, 3, 5 and 7.5	Stir	20 µm	5.6	75 BHN	450	Sajjadi <i>et al.</i> (2012)
2	AlMg4.5Mn/SiC	10 wt	Stir	35 µm	2	77 BHN	348	Rana <i>et al.</i> (2015)
3	Pure Al-SiC	3 wt	Vortex	80 µm	–	200 VHN	–	Mohammadpour <i>et al.</i> (2014)
4	AA 7075-TiC	8 wt	Stir	2 µm	4.25	202 VHN	–	Rao <i>et al.</i> (2014)
5	Al206-Al ₂ O ₃	5 vol	Stir	10 µm	14	–	–	Tahamtan <i>et al.</i> (2013)
6	AA7075-TiC	8 wt	Stir	2 µm	–	202.1 VHN	–	Ramakoteswara <i>et al.</i> (2016)
7	Al-12%Si + fly ash	15 wt	Stir	10 µm	–	74.8 BHN	–	Ramachandra and Radhakrishna (2007)
8	Al 6061 + K ₂ TiF ₆	8.1 wt	Ultrasonic assisted stir	50–100 µm	2.9	65 BHN	–	Gupta <i>et al.</i> (2018)
9	Al6061 + Fe ₂ O ₃ + B ₄ C	Fe ₂ O ₃ = 5 wt B ₄ C = 6 wt	Stir	Fe ₂ O ₃ = 5 µm B ₄ C = 10 µm	–	139 VHN	382	Mummoorthi <i>et al.</i> (2019)
10	Al6061 + tungsten carbide (WC) + Zircon sand	Al 11.6% Si alloy + Tungsten carbide 1.5% + zircon sand 1.5%	Stir	–	–	53.4 BHN	Load 117.55 kN	Vijaya Ramnath <i>et al.</i> (2018)
11	AA7075 + Si ₃ N ₄	0–8 wt	Stir	40 µm	–	140–145 VHN	800–900	Ul Haq and Anand (2018)
12	Al6061 + granite and graphite micro-fillers	Granite 4 wt, Graphite 2 wt	Stir	75 µm	–	106.4 BHN	–	Sharma <i>et al.</i> (2017)
13	AA 2618 + Si ₃ N ₄ , AlN, ZrB ₂	8 wt	Stir	100 µm	–	178 VHN	413	Selvaraj <i>et al.</i> (2017)
14	AA 2024 + fly ash particles	10 wt	Stir	–	8.75	–	950	Rao <i>et al.</i> (2012)
15	Al 2024 + Fly Ash and E-Glass	1 wt E-glass, 9 wt fly ash	Stir	Fly ash 40–100 µm, E-glass 2–3 mm length	–	51 BHN	400	Ramesh <i>et al.</i> (2018)
16	Al–Cu–Mg alloy + bagasse ash particles	10 wt	Stir	63 µm	–	60–70 BHN	450	Aigbodion <i>et al.</i> (2010)
17	Al6061 + B ₄ C _p	7 wt	Melt stirring	88 µm	2.322	120.5 VHN	360	Auradi <i>et al.</i> (2014)
18	AA2024 + Fly ash particles	10 wt	Stir	60 µm	–	131 VHN	950	Rao <i>et al.</i> (2011)
19	Al 2618 + Si ₃ N ₄ , AlN and ZrB ₂	8 wt	Stir	–	–	178 VHN	413	Mathan Kumar <i>et al.</i> (2016)
20	AA6351 + TiB ₂	8 wt	Direct melt reaction	–	–	82 VHN	220	Mohanavel <i>et al.</i> (2017)
21	A356 + B ₄ C	8 wt	Stir	63 µm	–	140 VHN	600	Motha and Majumder (2017)
22	Al wire + Al ₂ O ₃	10 wt	Stir	15–20 µm	–	98 BHN	250	Hallem <i>et al.</i> (2018)

23	Al 6063 + Weld slag	10 wt	Stir	50 μm	–	55 BHN	627	Paranthaman <i>et al.</i> (2019)
24	LM6 + ZrO_2	12 wt	Stir	1–10 μm	–	69.22 VHN	218	Karthikeyan and Jinu (2015)
25	Al6061 + BN	9 wt	Stir	–	–	85 VHN	–	Mukesh <i>et al.</i> (2018)
26	Al 7075 + B_4C	10 vol	Stir	16–20 μm	–	170 BHN	300	Baradeswaran and Elaya Perumal (2013)
27	Al6063 + ZrO_2 + Al_2O_3	5 wt ZrO_2 , 5 wt Al_2O_3	Stir	$\text{ZrO}_2 = 20 \mu\text{m}$ $\text{Al}_2\text{O}_3 = 30 \mu\text{m}$	–	91.1 VHN	685	Bhaumik and Maity (2016)
28	ADC12 + rice husk ash(RHA) + B_4C	12 wt RHA 5 wt B_4C	Stir	$\text{B}_4\text{C} = 40 \mu\text{m}$	–	98 VHN	567.29	Cardoso <i>et al.</i> (2014)
29	A357 + ZrO_2	10 vol	Squeeze	40–100 μm	1.237	136 VHN	716	Abou El-Khair (2011)
30	AA6061 + Cenosphere	5 vol	Stir	50–100 μm	–	57 VHN	212	Ilandjezian and Gopalakannan (2017)

Table 2 Properties of AMMCs produced through stir casting process using nanosize reinforcement

S. No.	Composites	Wt./ Vol. fraction (%)	Casting method	Particle size	Porosity (%)	Hardness	UCS (Mpa)	References
1	A356 (Al-Si7Mg)/Al ₂ O ₃	1, 2, 3 and 4	Stir	50 nm	2.4	72 BHN	630	Mišković <i>et al.</i> (2006)
2	Al-4.5 wt% Cu/Al ₂ O ₃	1.5	Stir	50 nm	2.1	92 HV	240 Yield	Valibeygloo <i>et al.</i> (2013)
3	AA7075 (Al-Zn6MgCu)/Al ₂ O ₃	1.2	Stir	50 nm	4.3	160 HV	760	Ezatpour <i>et al.</i> (2016)
4	A356 (Al-Si7Mg)/SiC	1	Stir	25–50 nm	–	–	110 Yield	Hamedan and Shahmiri (2012)
5	Al206 (Al-Cu5MnFe)-Al ₂ O ₃	5 vol	Stir	100 nm	4	–	–	Tahamtan <i>et al.</i> (2013)
6	Al7075 + Al ₂ O ₃ p	8 wt	Stir	40–50 nm	–	260 VHN	580	Rahman and Sirajudeen (2019)
7	Al2618 + B ₄ C	6 wt	Stir	500 nm	–	–	790	Bellamkonda <i>et al.</i> (2019)
8	AA7075 + ZrO ₂	4 wt	Stir	20–30 nm	–	–	745	Bellamkonda <i>et al.</i> (2019)
9	Al7075 + Al ₂ O ₃	1.5 wt	Ultrasonic assisted stir	80 nm	–	–	691	Chen and Yan (2015)
10	AA7075 + Si ₃ N ₄ , TaC and Ti	0.5 wt TaC, 0.25 wt Si ₃ N ₄ ,	Stir	Si ₃ N ₄ = 40.55 nm, TaC = 236.71 nm, Ti = 69.24 μm	–	137.79 VHN	624.54	Pradeep Kumar <i>et al.</i> (2018)
11	AA6061 + Al ₂ O ₃ + Si ₃ N ₄	45 wt Al ₂ O ₃	Stir	Al ₂ O ₃ = 50 μm, Si ₃ N ₄ = 40 nm	–	73 VHN	361.74	Hariharasakthisudhan and Jose (2018)

**Fig. 4** Compression stress–strain curves of fracture indication for LM25 + Al₂O₃ composite. Reproduced from Kumar, P., Victor, J., Arunachalam, R. *et al.*, 2019. Production of aluminum alloy-based metal matrix composites using scrap aluminum alloy and waste materials: Influence on microstructure and mechanical properties. *J. Alloys Compd.* 784, 1047–1061.

considered towards strengthening the lattice structure against various flow processes such as plastic flow, strengths at high temperature, and high rates of deformation (Lavernia and Schoenung, 2017).

In MMCs, based on the features of the reinforcement particles, which are secondary phases, the strengthening mechanisms can also be classified into direct and indirect. Direct strengthening is a result of the load transfer from the matrix to the reinforcement. In contrast, indirect strengthening is attributed to the impact that reinforcements may have on the microstructure or deformation mode of the matrix (Gnjidic *et al.*, 2001). Many microstructural variables within this scheme can have an impact on strengthening. These factors include matrix alloy, aging conditions, particle volume fraction, and particle size. Strengthening in MMCs has been related to dislocations of a very high density in the matrix originating from differential thermal contraction, geometrical constraints, and plastic deformation during processing (Ibrahim *et al.*, 1991). Based on this, the strength exhibited by the engineering

Table 3 Current applications of AMMCs

S.No.	Composite	Applications	Company	Reference
1	Al/SiC	Disc brakes for high-speed trains	Temponik	Temponik Test Functional Prototype (2015)
2	Al/SiC	Pistons	Ztotecki	Aluminum Matrix Composite (AMC) Pushrods (2018)
3	AA2009/SiC 15%	Fan exit guide vanes, F-16 ventral fins and fuel access covers	DWA	Alucoworld (2018)
4	6091/SiC 40% 6092/SiC 44%	Electronic packing	DWA	DWA–Aluminum Composites (2020)
5	Al75/SiC 25% Al70/SiC30 Al60/SiC40	Heat sinks, display types of equipment, semiconductor inspection parts.	Ferrotec	Ferrotec–Metal Matrix Composites (2020)
6	Al 30%/Al ₂ O ₃ 70%	Display equipment parts	Tesa	Tesa (2020)
7	Al/Nextel610/45f	Pushrods	3M	Aluminum Matrix Composite (AMC) Pushrods (2018)
8	Al 60%/Al ₂ O ₃ 40%	Cylinder sleeves in engines, piston-recess walls, brake pad backing plates, bearings, brake disks	CeramTec	CeramTec–The Ceram Expert (2020)
9	AA2024 (AlCu4Mg1)/SiC 25% AA6061 (AlMg1SiCu)/SiC 20% AA6061 (AlMg1SiCu)/SiC 40%	Outlet guide vanes Hydraulic blocks Wheels Fixed-wing structure/ skins Helicopter components Pistons Piston pins Cylinder liners Brake calipers Connecting rods Pushrods Valve train Chassis components Optical systems Sensors Satellite structures	Materion	SUPREMEX–Metal Matrix Composites – Lighter, Stiffer, Stronger (2020)
10	AA2024 (AlCu4Mg1)/Al ₂ O ₃	Turbo impeller Heat sink Stator vane Piston head Timing wheel	Elementum 3D	Elementum–Aluminum (2020)
11	Al/SiC Al/B ₄ C Al/Al ₂ O ₃	Precision equipment components, thermal management base plates, mirrors, optical housings, armor, brake rotors, connecting rods, and pistons	M Cubed Technologies	Ceramics and Metal Matrix Composites (2020)
12	Al/Al ₂ O ₃ (nano)	Piston Connecting rods Aerospace Armor	Gamma Alloys	Gamma Alloys (2016)

Source: Arunachalam, R., Kumar, P., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *J. Manuf. Process.* 42, 213–245.

or engineered materials is generally attributed to five different theories: Orowan, Hall–Petch, load transfer strengthening from the soft matrix to hard and tough reinforcement, Taylor strengthening (Huang *et al.*, 2019), and fracture strengthening. **Table 4** summarizes these different strengthening models.

The key mechanism in improving strength, especially with nano-scale reinforcement, is the Orowan strengthening. The reinforcement particles serve as an obstruction, preventing the dislocation movement, leading to a pile-up of dislocations. Such dislocations, bows, and bypasses the reinforcement by creating loops around them known as Orowan strength looping (Huang *et al.*, 2019). The Orowan strengthening mechanism is schematically illustrated in **Fig. 5**. Dislocations distort the crystal locally,

Table 4 Strengthening modes of AMMCs

S. No.	Strengthening models	Strengthening mechanism	Governing equation	References
1	Hall-Petch	Nanoparticles strengthen a material by pinning grain boundaries during thermomechanical processing resulting in smaller grain sizes which enhances the strength	$\Delta\sigma_{HP} = K_{HP} [D_f^{-1/2} - D_o^{-1/2}]$ where K_{HP} is the Hall-Petch slope, D_f is the average grain size of the composite and D_o the average grain size of as-cast alloy $\sigma_y = \sigma_0 + k_y d^{-1/2}$ where σ_y is the yield strength of the composite, σ_0 and k_y are the constants	Zhang <i>et al.</i> (2015) Huang <i>et al.</i> (2019)
2	Load bearing	Stiffer reinforcement phase will sustain higher local stress than the less rigid matrix	$\Delta\sigma_{LT} = \frac{1}{2} \sigma_{ym} V_f$ $\Delta\sigma_{LT} = \sigma_m [1/(2m)]$ where σ_m is yield stress of matrix and m is the volume fraction of reinforcement	Yang <i>et al.</i> (2017) Mirza and Chen (2015) Huang <i>et al.</i> (2019)
3	Orowan	Dispersion strengthening from the reinforcement particles	$\Delta\sigma_{Orowan} = \beta \frac{0.4 G_m b}{\pi \lambda} \left[\frac{\ln \left(\frac{d_p}{b} \right)}{(1 - \nu_m)^{1/2}} \right] \lambda = d_p \left[\sqrt{\frac{\pi}{4 V_f}} - 1 \right]$ $\Delta\sigma_{Orowan} = \frac{G b}{2\pi \sqrt{1 - \nu} [(0.779/\sqrt{f}) - 0.785] d} \ln \frac{0.785 d}{b}$ where G is shear modulus, b is burger vector, ν is the Poisson ratio, d is the grain size, f is the volume fraction of reinforcement.	Zhang and Chen (2006) Huang <i>et al.</i> (2019)
4	Taylor	The difference in coefficient of thermal expansion between matrix and reinforcement	$\Delta\sigma_{Taylor} = \sqrt{3} \varphi G_m b \left[\frac{12 V_f \Delta\alpha \Delta T}{b(1 - V_f) d_p} + \frac{8 V_{f,p}}{b d_f} \right]^{1/2}$ where b is burger vector of the matrix, φ is Taylor factor, ΔT is the difference in processing temperature and ambient temperature, d_p mean diameter of the reinforced particles, G_m is the shear modulus of the matrix, V_f is the volume fraction of the reinforced particles and $\Delta\alpha$ is thermal mismatch difference between matrix and reinforcement	Ibrahim <i>et al.</i> (1991), Chelliah <i>et al.</i> (2017)
5	Fracture strengthening	Fracture strengthening is to boost the fracture toughness of a material, which leads to an increase in strength. It is a combined effect of plastic dissipation and energy spent to start crack	$U_n = \frac{2G_f^1}{\sigma_f}$ where G_f^1 is the energy required to open the unit area of the crack. $2G_f^1 = \frac{K_{IC}^2}{E^j}$ where K_{IC} and E^j are the fracture toughness and effective Young's modulus of CNTs, respectively. The plastic deformation can be determined by using Johnson-Cook constitutive model equation $\bar{\sigma} = A + B \varepsilon^n$ where $\bar{\sigma}$ is the effective stress, ε is the plastic strain, A, B, and n are the yield strength, hardening modulus and coefficient of hardening respectively	Huang <i>et al.</i> (2019)

Source: Chelliah, N.M., Singh, H., Surappa, M.K., 2017. Microstructural evolution and strengthening behavior in in-situ magnesium matrix composites fabricated by solidification processing. Mater. Chem. Phys. 194, 65–76.

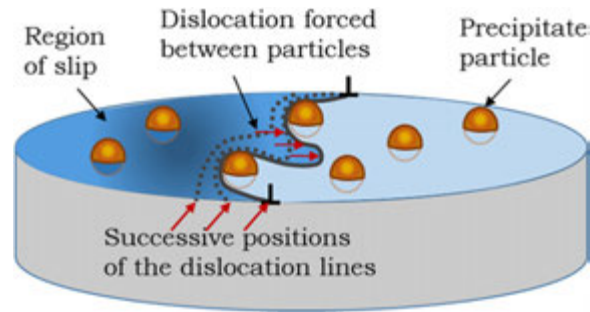


Fig. 5 Schematic representation of Orowan strengthening mechanism (dispersion hardening). Reproduced from Ashby, M.F., Ferreira, P.J., Schodek, D.L., 2009. Chapter 4 – Material classes, structure, and properties. *Nanomaterials, Nanotechnologies and Design*. Elsevier, pp. 87–146.

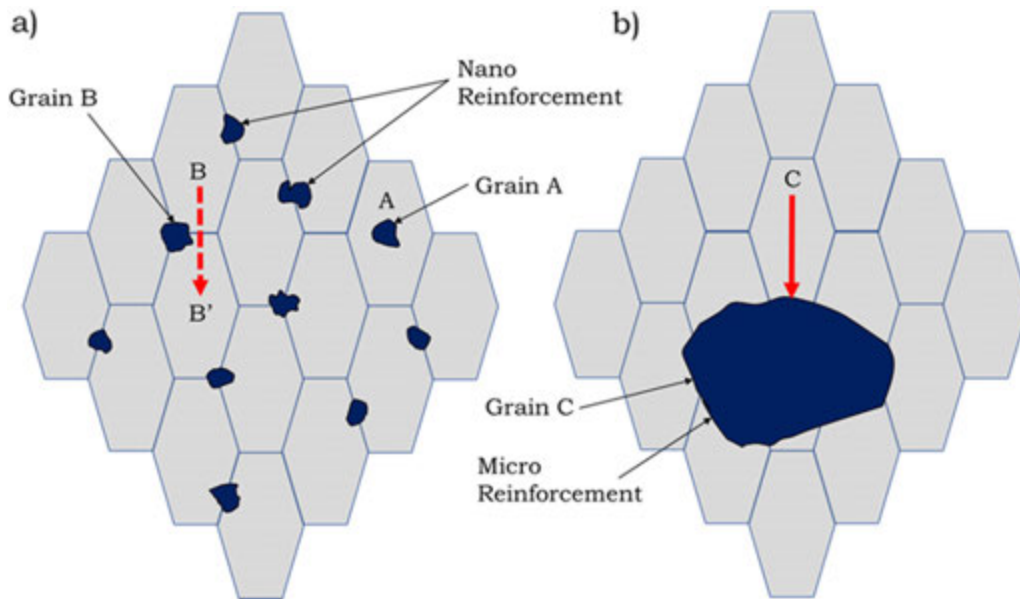


Fig. 6 Schematic representation of load transfers for (a) nano-reinforced matrix metal, and (b) micro-reinforced matrix metal. Reproduced from Yang, H., Jiang, L.I.N., Balog, M., Krizik, P., Schoenung, J.M., 2017. Reinforcement size dependence of load bearing capacity in ultrafine-grained metal matrix composites. *Metall. Mater. Trans. A* 48, 4385–4392.

and the resulting energy is correlated with the local distortion. It gives the dislocation a line tension equal to the surface tension of a liquid. Stronger and more obstacles block the movement much more effectively because when substantial barriers are in its direction, the dislocation must bend between and around them, and thus the duration of the dislocation increases, as shown in Fig. 5. When the length of the dislocation line increases, the energy also increases, and this energy increases the stress required to distort the surface and strengthens the material. If the particles are far-off, the length of the line decreases with a decrease in strength. When both the size and the space of the dispersed particles are nano-dimensional, the change in strength is substantial (Ashby *et al.*, 2009).

Grain boundary strengthening is otherwise called a Hall–Petch strengthening model, which is a commonly accepted mechanism for the higher strength of AMMCs. According to the Hall–Petch effect, the strength is improved with the decrease in the grain size of the matrix (Huang *et al.*, 2019).

Load bearing is another process by which the reinforcement particles could reinforce a material. Fig. 6 shows a schematic illustration of the role of the various microstructures and interfaces in the potential load transfer for the vertical load applied (Yang *et al.*, 2017). The figure illustrates a simplified case of B_4C in an aluminum matrix, and the actual stress state could be quite complex in the actual material. In most microstructures, nano-reinforcement particles are mainly found at the grain boundary, triple point, and inside grain interiors. If nano-reinforcement particles are placed inside the grain, as shown in Fig. 6(a), the nano-reinforcement particles will stiffen the material. However, if nano-reinforcement particles are positioned at the grain boundary, the stress being transferred from Grain B will be transferred to Grain B' as shown by the dashed arrow. Fig. 6(b) illustrates the load-bearing mechanism of strengthening in the case of micro-reinforcement particles. If stress is transferred from Grain C, it must be

transferred to the micro-reinforcement particle because there is no adjacent matrix grain in the loading direction, as shown by the red arrow.

In Taylor strengthening mechanism, the volumetric strain occurs in the composite due to significant differences in coefficient of thermal expansion (CTE) between the matrix and the reinforced particles. To accommodate this CTE difference, dislocations are generated around the particles, thus increasing the flow stress in the matrix, which in turn increases the yield strength of the matrix (Gupta *et al.*, 2018).

Raj (2018) investigated the effect of reinforcing B_4C by conducting tensile testing on strengthening composites' behavior. The author has quantitatively analyzed the strengthening mechanisms and evaluated as a function of particle size and volume fraction. The yield strength of the composite rises considerably as the reinforcement particle was increased from 0 to 20 vol%. At a higher volume fraction of B_4C , the effect of thermal dislocation strengthening becomes more dominant as compared to other mechanisms (Raj, 2018).

The rapid cooling rate strengthens the alloy by preventing slipping. Srivatsan *et al.* (1995) implemented a quick cooling rate strategy. They obtained better high-temperature characteristics in aluminum alloys as a result of the growth of rapid solidification through the strengthening of the aluminum alloy matrix, which would fulfill the need for better high-temperature characteristics (Srivatsan *et al.*, 1995). Load bearing is not the only process by which the reinforcement particles can strengthen the material. When the reinforcement particles are tiny enough, they can reinforce the material by preventing the movement of the dislocation through the Orowan bowing. The grain boundary region can be improved by refining the components of aluminum alloy, which further increases the resistance to dislocation movement, enhancing the matrix yield strength. By using the Hall–Petch relationship, this increase in yield strength due to grain refinement can be calculated. Subsequently, thermomechanical processing of submicron-sized particles can contribute to the strengthening of Orowan in both coarse grain and ultra-fine grain regions (Zhang *et al.*, 2015). Matrix phase refining leads to the strengthening of the composites. During deformation, the grain boundaries effectively resist dislocation movement. The generation of dislocation density around the reinforcement particle due to difference in the coefficient of thermal expansion between matrix and reinforcement improves the hardness of the composites (Gupta *et al.*, 2018). Precipitates formed in the matrix also hamper dislocation motion. The dislocation on interaction with the precipitate is first bent due to the stress, then reconnected, and finally, the dislocation loops are formed around the particles. These dislocation loops hamper the motion of subsequently shaped dislocations and thus enhance the composite strength. In the micromechanics approach, the yield strength of the metal matrix can be calculated by considering the strengthening of grain refinement and Orowan strengthening.

Failure Modes of AMMCs

During the application of external loads, particle reinforced aluminum metal matrix composites exhibit different failure modes such as (1) the cracking of reinforcement particle (2) ductile failure by the void nucleation (3) interfacial debonding between the matrix and the reinforcement, and (5) matrix cavitation. An understanding of the mechanism of these failure modes is essential for improving the mechanical performance of metal–matrix composites for use in various engineering applications.

Particle Cracking

As per the fundamental theory of elasticity, the stress and strain patterns created at the initial loading point do not alter qualitatively during elastic loading but increase proportionally as the external load increases. On further loading, the plastic deformation in the matrix would lead to stress relaxation in the particles, which would delay the initiation of cracking in the material (Romanova *et al.*, 2009). The proportion between the bonding interface and the cracking of the particle relies on the form of the particle, the loading conditions, and the strength of the interface. In spherical solids, debonding dominates the cracking of the particles, while irregularly formed reinforcements display a scheme of cracking through the surface of the bulk. Debonding in compression manifests itself as individual patches, which are considered to be voids. These areas are sites of crack nucleation. When the cracks are further loaded, it spreads to the bulk of the particle (Romanova *et al.*, 2009).

Wu *et al.* (2016) synthesized and analyzed Al 7075/ B_4C composites with three different sizes of B_4C particles. The fracture mechanism is shown schematically in Fig. 7. Fig. 8 shows the SEM image of the fractured surface of the composite after compression testing. Micro-cracks were observed in the coarse B_4C powder. Pre-existing micro-cracks in B_4C particles continue to provide sites for crack nucleation and propagation. The rapid proliferation of micro-cracks leads to a surface fracturing with relatively low stress and limited macroscopic plastic deformation (Wu *et al.*, 2016).

For all particles, the first crack appears near the interface owing to the concentration of stress in adjacent boundary regions. Particle cracking at the interfaces increased with reinforcement content in the Al alloy (2014) matrix reinforced with Al_2O_3 (Srivatsan, 1996). Due to the intrinsic brittleness of the Al_2O_3 reinforcing particles combined with the tendency for it to fracture due to localized deformation results in particle cracking and particle–matrix interface debonding.

Gnjidic *et al.* (2001) researched the impact of SiC particles on the CW67 Al alloy and studied the compressive characteristics of the metal matrix composites produced by hot pressing. The research proved that the addition of SiC particles improved the yield strength and elastic modulus while reducing the ultimate compressive strength and ductility of the CW67 alloy in both peak-aged and under-aged circumstances. Adding larger size SiC particles contributes to cracking and adverse effects on the strengthening of

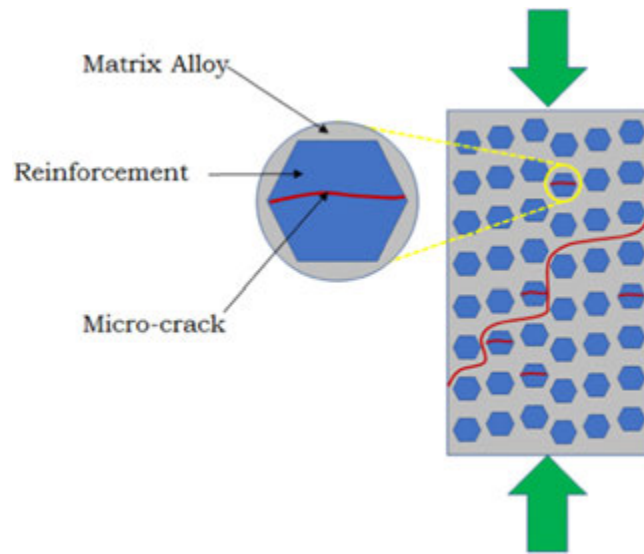


Fig. 7 Schematic representation of fracture mechanism. Reproduced from Wu, C., Ma, K., Wu, J. *et al.*, 2016. Influence of particle size and spatial distribution of B_4C reinforcement on the microstructure and mechanical behavior of precipitation strengthened Al alloy matrix composites. *Mater. Sci. Eng. A* 675, 421–430.

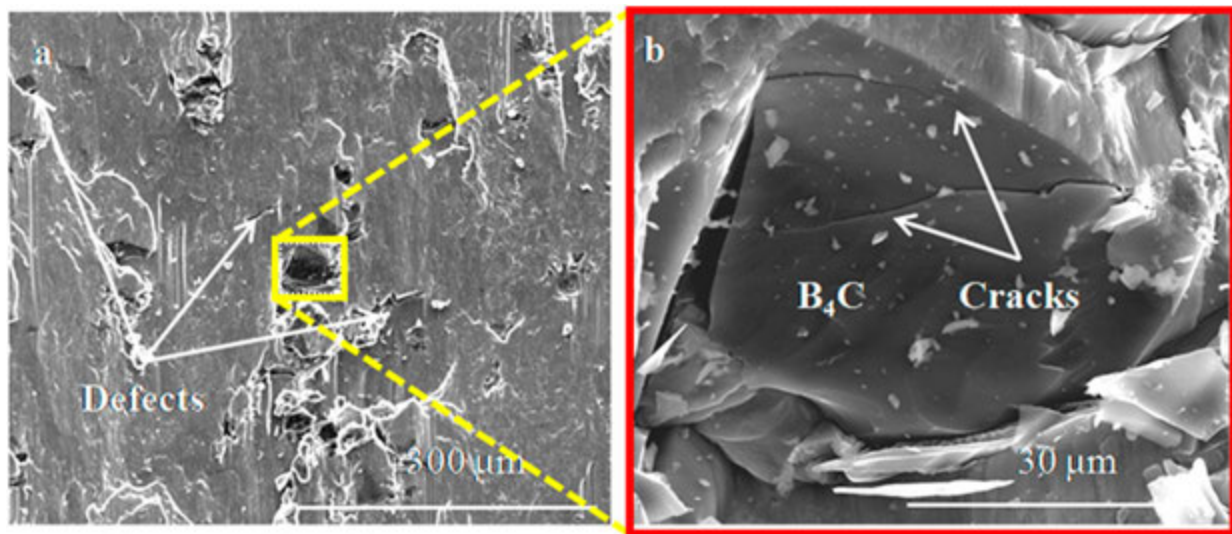


Fig. 8 SEM fractography of boron carbide cracking. Reproduced from Wu, C., Ma, K., Wu, J., *et al.*, 2016. Influence of particle size and spatial distribution of B_4C reinforcement on the microstructure and mechanical behavior of precipitation strengthened Al alloy matrix composites. *Mater. Sci. Eng. A* 675, 421–430.

CW67 alloys. Compared to the under-age matrix, higher compressive strength and decreased ductility were obtained with the peak-age matrix. The presence of SiC particles caused the aging process to accelerate due to an increase in the dislocation density, which created more sites for precipitate nucleation (Gnjidic *et al.*, 2001).

The smaller particles had a higher impact on the strengthening of the matrix than the bigger particles. One possible reason may be that a damaged larger size particle generates a higher concentration of micro void than a damaged smaller particle. As a result, they would be anticipated to have significant surface defects. This observation is attributed to the enhanced probability that larger size SiC particles would be more probable to have a critical size defect causing a fracture at a specified stress point. In the event of larger particle sizes and larger interparticle spacing, the contribution of residual thermal stress is likely to be relatively insignificant, as is any reinforcement due to enhanced dislocation density. Therefore, a decrease in yield stress and elastic modulus can be anticipated. Besides, the fracture will continue to accumulate after yield, leading to rapid failure and reduced strength and ductility than would have been the case with a composite comprising smaller SiC particles. As a result, the percentage increase in strengthening achieved with a composite comprising larger size SiC particles is lower than that achieved with one containing

smaller size particles. The existence of SiC particles may be damaging to the ultimate compressive strength of the composite materials due to the addition of possible failure mechanisms such as unreinforced aluminum alloy cracking, particle–matrix debonding and particle agglomeration. The particle cracking has a significant impact on the ultimate compressive strength of SiC/Al composite products. Also, the likelihood of reinforcement cracking rises with an increase in particle size.

Void Nucleation

Voids are created by the debonding of the reinforcement from the matrix material (Kumar *et al.*, 2019). In all the composites that were produced and were reinforced with alumina as well as spent alumina catalyst, voids appeared due to debonding of the reinforcement particles from the matrix. The SEM Fig. 9 with the inset image shows a typical void created by the debonding of the reinforcement. The voids dimensions matched with the average reinforcement particle size of 50 and 150 mm for alumina and spent alumina catalysts, respectively. These voids are typically caused by the poor wetting of the reinforcement with the matrix, as well as weak interfacial bonding (Kumar *et al.*, 2019).

Lewandowski *et al.* (1989) studied the effects of matrix microstructure on the tensile fracture surface. They identified void nucleation below the tensile fracture surface of an over-aged SiC particulate reinforced AMMC (Lewandowski *et al.*, 1989). Sahoo and Koczak (1991)

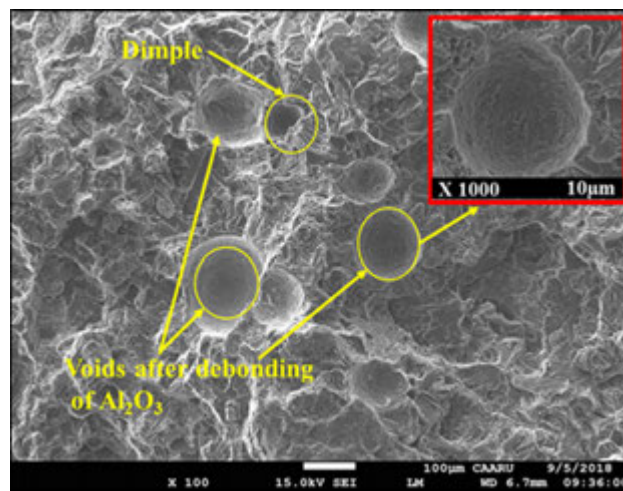


Fig. 9 SEM image of fracture surface morphology after tensile testing of scrap aluminum alloy wheel and Al_2O_3 . Reproduced from Kumar, P., Victor, J., Arunachalam, R. *et al.*, 2019. Production of aluminum alloy-based metal matrix composites using scrap aluminum alloy and waste materials: Influence on microstructure and mechanical properties. *J. Alloys Compd.* 784, 1047–1061.

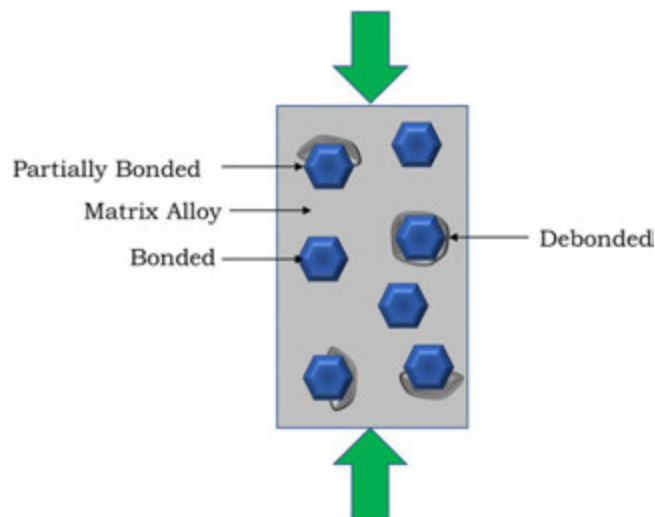


Fig. 10 Schematic representation of bonded and debonded interfaces of reinforcement particle in the matrix. Reproduced from Cho, Y.J., Kang, Y., Lee, Y.C., Park, Y., Lee, W., 2017. Influence of partially debonded interface on elasticity of syntactic foam: A numerical study. *Materials* 8, 1–15.

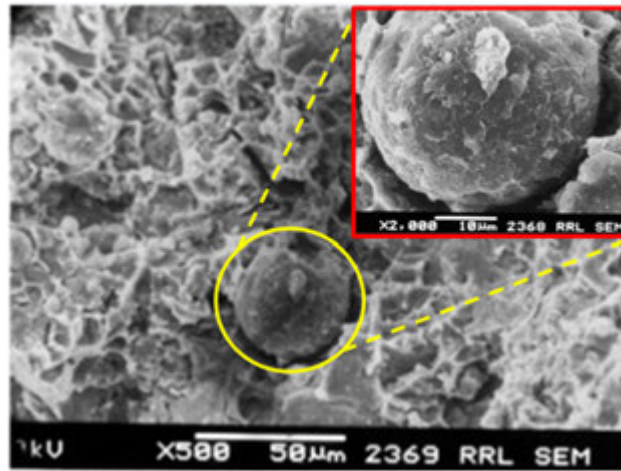


Fig. 11 Interfacial debonding of reinforcement from the matrix. Reproduced from Rajan, T.P.D., Pillai, R.M., Pai, B.C., Satyanarayana, K.G., Rohatgi, P.K., 2007. Fabrication and characterization of Al-7Si-0.35Mg/fly ash metal matrix composites processed by different stir casting routes. *Compos. Sci. Technol.* 67, 3369–3377.

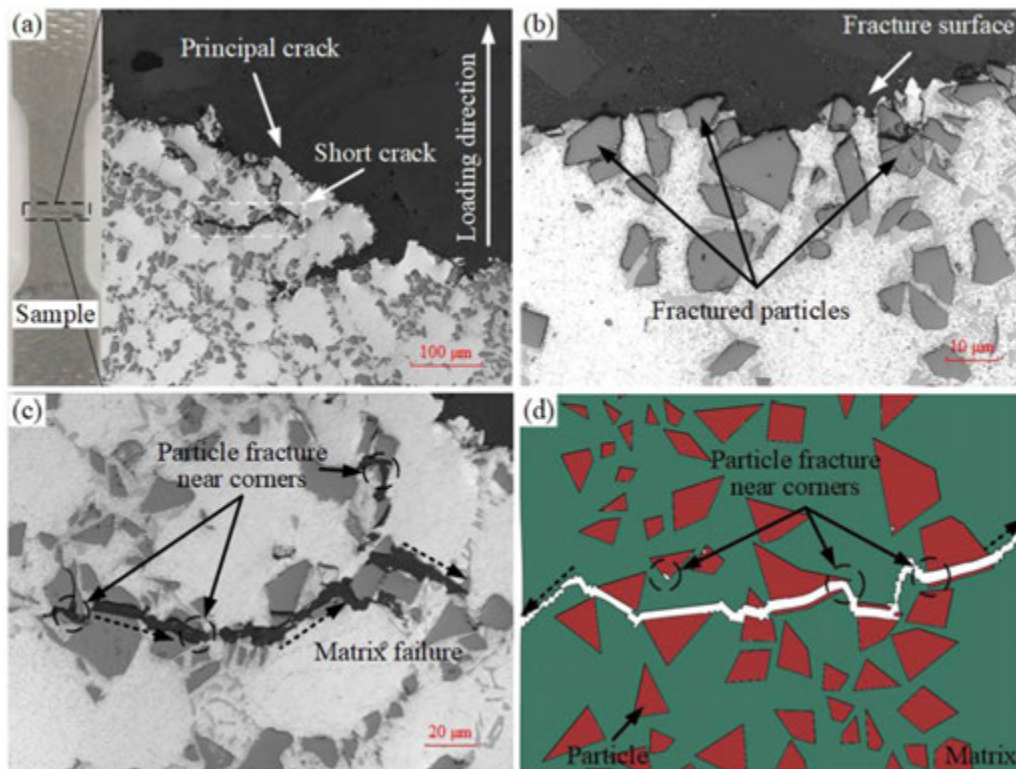


Fig. 12 Cross-section images of the fractured specimen: (a) General view; (b) enlarged view of the fractured surface; (c) enlarged view of the short cracks, and (d) fractured surface predicted by the microstructure-based model. Reproduced from Wu, Q., Xu, W., Zhang, L., 2019. Microstructure-based modeling of fracture of particulate reinforced metal matrix composites. *Compos. Part B Eng.* 163, 384–392.

investigated the effect of microstructure on the tensile fracture surface of TiC reinforced AMMC, which indicated ductile failure and sites for void nucleation (Sahoo and Koczak, 1991).

Interfacial Debonding

Matrix/reinforcement interfacial debonding is also one of the characteristic features of the fracture process. The schematic representation of bonded and debonded interfaces of reinforcement particles in the matrix is shown in Fig. 10.

Ozden *et al.* (2007) investigated the impact strength, microstructural, and fractographic analysis of SiC particle reinforced AMMC at different temperature conditions. The failure took place in the matrix or near the particle–matrix interface as debonding at between 200 and 300°C temperatures. When there is a failure of debonding in the particle–matrix interface, the impact strength of composites decreases significantly (Ozden *et al.*, 2007).

Rajan *et al.* (2007) investigated the microstructural and properties fly ash particle reinforced AMMC through different casting routes. They observed a significant reduction in tensile strength in fly ash composites, due to interfacial debonding. Fig. 11 shows the tensile fractography exhibiting a mixed-mode of fracture: Ductile fracture for the aluminum matrix and brittle fracture for the fly ash particle, and the inset figure shows clearly the partially debonded reinforcement particle (Rajan *et al.*, 2007).

Matrix Cavitation (Failure)

Cavitation in the matrix reduces the MMC's ductility as these cavities (voids) reduce the constraint on the plastic flow between the voids, thus encouraging flow localization and void coalescence. Voids usually nucleate when local tensile stress through an interface such as inside a particle, or when the matrix exceeds interfacial bond strength (interfacial decohesion), particle fracture stress (particle cracking), or matrix cavitation stress (matrix failure), respectively (Tham and Cheng, 2001). Whitehouse and Clyne (1993) observed cavitation development in the Al₂O₃ reinforced AMMC during tensile testing. The cavities are usually formed in the matrix adjoining the reinforcement, and approximately in line with the axis of the applied stress (Whitehouse and Clyne, 1993). Wu *et al.* (2019) developed a microstructure-based model to explain the material deformation and fracture of A359/SiC metal matrix composite. The fractured samples after the tensile tests were polished carefully, and Fig. 12(a)–(c) shows their typical microstructures. The light gray area is the matrix, and the dark gray zones are the reinforcement particles. In order to compare with the results of the microstructure-based model, an enlarged image that was obtained from the simulation is shown in Fig. 12(d). It can be seen that the particle fractures near its sharp corners because of stress and strain concentrations. The matrix surrounding the fracture particles fails around the crack tips, either by connecting the fractured particles or propagating along the tension direction (Wu *et al.*, 2019).

Conclusions

In this article, we have provided a comprehensive overview of AMMCs right from production to analysis of the strengthening mechanisms as well as failure modes of composite materials. Stir-squeeze casting is one of the most straightforward and established processes for the production of AMMCs through the liquid state processing route is discussed, and the recommended process parameters are proposed. With the advent of nanomaterials in the last decade, metal matrix nanocomposites with exceptional mechanical properties have been developed for promising applications in the automotive and aerospace sectors. The compressive strength of AMMCs is the main focus since hardly literature has focussed on this aspect of composites. AMMCs have been successfully produced through stir casting process with ultimate compressive strength ranging from 700 to 800 MPa even with relatively less than 5% weight percentage of nanosize reinforcement particles as compared to micro-sized reinforcement particles. The strengthening of AMMCs usually occurs through five different mechanisms: Orowan, Hall–Petch, load-bearing, Taylor, and fracture strengthening. Likewise, the composite materials can fail through any of these standard failure modes such as cracking of reinforcement particle, ductile failure by the void nucleation, interfacial debonding between the matrix and the reinforcement and matrix cavitation. Thus this article is expected to provide a far-reaching domain knowledge on the various aspects of AMMCs, especially concerning strengthening mechanisms and failure modes. The understanding of the strengthening mechanisms and the failure modes will significantly contribute to the production of quality AMMCs for high performance future industrial applications.

References

- Abou El-Khair, M.T., 2011. Effect of squeeze pressure on microstructure, aging and mechanical properties of A357/ZrO₂ composite. *Int. J. Eng. Res. Africa* 4, 59–66.
- Aigbodion, V.S., Hassan, S.B., Ogheneweta, J.E., 2010. Microstructural analysis and properties of Al–Cu–Mg/bagasse ash particulate composites. *J. Alloys Compd.* 497, 188–194.
- Aktaş, S., Anil, E., 2018. A review on the effects of micro-nano particle size and volume fraction on microstructure and mechanical properties of metal matrix composites manufactured via mechanical alloying. *Int. Adv. Res. Eng. J.* 2, 68–74.
- Alucoworld, 2018. Aluminum Composite Panel Manufacturer (WWW document). Available at: <http://www.alucoworld.com/products> (accessed 04.04.18).
- Aluminum Matrix Composite (AMC) Pushrods, 2018. 3M Science. Applied to Life (WWW document). Available at: <http://solutions.3m.com/3MContentRetrievalAPI/BlobServlet?Lmd=1149596328000> (accessed 01.01.18).
- ASTM, 2010. Standard Test Methods of Compression Testing of Metallic Materials at Room Temperature: Annual Book of ASTM Standards. ASTM.
- Arunachalam, R., Kumar, P., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *J. Manuf. Process.* 42, 213–245.
- Ashby, M.F., Ferreira, P.J., Schodek, D.L., 2009. Chapter 4 – Material classes, structure, and properties. In: *Nanomaterials, Nanotechnologies and Design*. Elsevier, pp. 87–146.
- Auradi, V., Rajesh, G.L., Kori, S.A., 2014. Preparation and evaluation of mechanical properties of 6061Al–B₄Cp composites produced via two-stage melt stirring. *Mater. Manuf. Process.* 29, 194–200.
- Baradeswaran, A., Elaya Perumal, A., 2013. Influence of B₄C on the tribological and mechanical properties of Al 7075–B₄C composites. *Compos. Part B Eng.* 54, 146–152.

- Bellamkonda, P.N., Sudabathula, S., Srikanth, V.M., Rajesh, A., 2019. Wear and electrochemical corrosion behaviour of nano ZrO_2 reinforced AA7075 metal matrix composites. *Int. J. Mech. Prod. Eng. Res. Dev.* 9, 793–802.
- Bhaumik, M., Maity, K., 2016. Fabrication and characterization of the $\text{Al6063/5\%ZrO}_2/5\%\text{Al}_2\text{O}_3$ composite. *J. Phys. Conf. Ser.* 755.
- Bhat, T.B., Arunachalam, V.S., 1980. Strengthening mechanisms in alloys. *Prec. Indian Acad. Sci. (Engg. Sci.)* 3, 275–296.
- Cardoso, K.R., Muñoz-Morris, M.A., Lieblich, M., Morris, D., 2014. Effect of equal channel angular pressing (ECAP) on microstructure and properties of Al-FeAlCr intermetallic phase composites. *Mater. Res.* 17, 775–780.
- Ceramics and Metal Matrix Composites, 2020. II-VI-Materials That Matters (WWW Document). Available at: <https://www.ii-vi.com/ceramics-and-metal-matrix-composites/> (accessed 29.03.2020).
- CeramTec—The Ceram Expert, 2020. Ceramic Seal Rings, Bearings and Sealing Technology in Automotive Engineering (WWW document). Available at: <https://www.ceramtec.com/applications/seal-rings-bearings-seals/automotive-engineering/> (accessed 29.03.2020).
- Chelliah, N.M., Singh, H., Surappa, M.K., 2017. Microstructural evolution and strengthening behavior in in-situ magnesium matrix composites fabricated by solidification processing. *Mater. Chem. Phys.* 194, 65–76.
- Chen, X.H., Yan, H., 2015. Effect of nanoparticle Al_2O_3 addition on microstructure and mechanical properties of 7075 alloy. *Int. J. Cast Met. Res.* 28, 337–344.
- Dao, V., Zhao, S., Lin, W., Zhang, C., 2012. Effect of process parameters on microstructure and mechanical properties in AlSi9Mg connecting-rod fabricated by semi-solid squeeze casting. *Mater. Sci. Eng. A* 558, 95–102.
- Dhanashekar, M., Senthil Kumar, V.S., 2014. Squeeze casting of aluminium metal matrix composites – An overview. *Procedia Eng.* 97, 412–420.
- DWA—Aluminium Composites, 2020. Highly Loaded Al MMCs (WWW document). Available at: <https://www.dwa-usa.com/al-mmc-material-systems.html> (accessed 29.03.2020).
- Elementum—Aluminium, 2020. 3D Printed Aluminum Elementum 3D Products (WWW document). Available at: <https://www.elementum3d.com/aluminum-mmc> (accessed 29.03.2020).
- Ezatpour, H.R., Torabi Parizi, M., Sajjadi, S.A., Ebrahimi, G.R., Chaichi, A., 2016. Microstructure, mechanical analysis and optimal selection of 7075 aluminum alloy based composite reinforced with alumina nanoparticles. *Mater. Chem. Phys.* 178, 119–127.
- Ferrotech – Metal Matrix Composites, 2020. Metal Matrix Composite Advanced Ceramics (WWW document). Available at: <https://ceramics.ferrotec.com/products/metal-matrix/> (accessed 29.03.2020).
- Gamma Alloy, 2016. The Next Generation of Lightweight Alloys—Nanotechnology Inside Every Bar (WWW document).
- Gloria, A., 2019. Alloys for aeronautic applications: State of the art and perspectives. *Metals* 9, 1–26.
- Gnjidic, Z., Bozic, D., Mitkov, M., 2001. The influence of SiC particles on the compressive properties of metal matrix composites. *Mater. Charact.* 47, 129–138.
- Gupta, R., Chaudhari, G.P., Daniel, B.S.S., 2018. Strengthening mechanisms in ultrasonically processed aluminium matrix composite with in-situ Al_3Ti by salt addition. *Compos. Part B Eng.* 140, 27–34.
- Hallem, A.H., Jasim, T.A., Radhi, N.S., 2018. Effect of alumina reinforcement on some mechanical properties of aluminum matrix composites produced by stir casting process. *Int. J. Civ. Eng. Technol.* 9, 1271–1280.
- Hamedan, A.D., Shahmiri, M., 2012. Production of A356–1 wt% SiC nanocomposite by the modified stir casting method. *Mater. Sci. Eng. A* 556, 921–926.
- Hariharasakthisudhan, P., Jose, S., 2018. Influence of metal powder premixing on mechanical behavior of dual reinforcement (Al_2O_3 (μm)/ Si_3N_4 (nm)) in AA6061 matrix. *J. Alloys Compd.* 731, 100–110.
- Huang, S.J., Abbas, A., Ballóková, B., 2019. Effect of CNT on microstructure, dry sliding wear and compressive mechanical properties of AZ61 magnesium alloy. *J. Mater. Res. Technol.* 8, 4273–4286.
- Ibrahim, I.A., Mohamed, F.A., Lavernia, E.J., 1991. Particulate reinforced metal matrix composites – A review. *J. Mater. Sci.* 26, 1137–1156.
- Ilandjezian, R., Gopalakannan, S., 2017. Tensile fracture and compression failure behavior of cenosphere reinforced AA6061 metal matrix composite. *Procedia Eng.* 173, 1239–1245.
- Jo, M.C., Choi, J.H., Yoo, J., *et al.*, 2019. Novel dynamic compressive and ballistic properties in 7075-T6 Al-matrix hybrid composite reinforced with SiC and B_4C particulates. *Compos. Part B Eng.* 174, 107041.
- Karthikeyan, G., Jinu, G.R., 2015. Experimental investigation on mechanical and wear behaviour of aluminium LM6/ ZrO_2 composites fabricated by stir casting method. *J. Balk. Tribol. Assoc.* 21, 539–556.
- Kumar, P., Victor, J., Arunachalam, R., *et al.*, 2019. Production of aluminum alloy-based metal matrix composites using scrap aluminum alloy and waste materials: Influence on microstructure and mechanical properties. *J. Alloys Compd.* 784, 1047–1061.
- Lavernia, E.J., Schoenung, J.M., 2017. Particulate reinforced aluminium alloy matrix composites – A review on the effect of microconstituents. *Adv. Mater. Sci.* 48, 91–104.
- Lewandowski, J.J., Liu, C., Hunt Jr, W.H., 1989. Effects of matrix microstructure and particle distribution on fracture of an aluminum metal matrix composite. *Mater. Sci. Eng. A* 107, 241–255.
- Lim, C.S., Clegg, A.J., 1997. The production and evaluation of metal-matrix composite castings produced by a pressure-assisted investment casting process. *J. Mater. Process. Technol.* 67 (1–3), 13–18.
- Maleki, A., Niroumand, B., Shafiei, A., 2006. Effects of squeeze casting parameters on density, macrostructure and hardness of LM13 alloy. *Mater. Sci. Eng. A* 428, 135–140.
- Mathan Kumar, N., Senthil Kumar, S., Kumaraswamidhas, L.A., 2016. Aerospace application on Al 2618 with reinforced – Si_3N_4 , AlN and ZrB_2 in-situ composites. *J. Alloys Compd.* 672, 238–250.
- Mirza, F.A., Chen, D.L., 2015. A unified model for the prediction of yield strength in particulate-reinforced metal matrix nanocomposites. *Materials* 8, 5138–5153.
- Mišković, Z., Bobić, I., Tripkovic, S., Rac, A., Vencel, A., 2006. The structure and mechanical properties of an aluminium A356 alloy base composite with Al_2O_3 particle additions. *Tribol. Ind.* 28, 23–27.
- Mohammadpour, M., Azari Khosroshahi, R., Taherzadeh Mousavian, R., Brabazon, D., 2014. Effect of interfacial-active elements addition on the incorporation of micron-sized SiC particles in molten pure aluminum. *Ceram. Int.* 40, 8323–8332.
- Mohanavel, V., Rajan, K., Arul, S., Senthil, P.V., 2017. Production, microstructure and mechanical behavior of AA6351/ TiB_2 composite synthesized by direct melt reaction method. *Mater. Today Proc.* 4, 3315–3324.
- Motha, C., Majumder, M.C., 2017. Investigation of tribological and mechanical properties of aluminium boron carbide composites using response surface methodology and desirability analysis. *Ind. Lubr. Tribol.* 56, 5.
- Mukesh, Y.B., Bharathesh, T.P., Keshavamurthy, R., Girish, H.N., 2018. Impact of extrusion procession wear behavior of boron nitride reinforced aluminum 6061- based composites. *Int. J. Mech. Prod. Eng. Res. Dev.* 8, 873–882.
- Mummoorthi, D., Rajkumar, M., Ganesh Kumar, S., 2019. Advancement and characterization of Al-Mg-Si alloy using reinforcing materials of Fe_2O_3 and B_4C composite produced by stir casting method. *J. Mech. Sci. Technol.* 33, 3213–3222.
- Nturanabo, F., Masu, L., Kirabira, J.B., 2019. Chapter 5 - Novel applications of aluminium metal matrix composites. In: Cooke, K. (Ed.), *Aluminum Alloys and Composites*. IntecOpen, pp. 1–24.
- Okayasu, M., Takeuchi, S., Shiraishi, T., 2013. Corrosion and mechanical properties of cast aluminium alloys. *Int. J. Cast Met. Res.* 26, 319–330.
- Ozden, S., Ekcici, R., Nair, F., 2007. Investigation of impact behaviour of aluminium based SiC particle reinforced metal–matrix composites. *Compos. Part A Appl. Sci. Manuf.* 38, 484–494.
- Panwar, N., Chauhan, A., 2018. Fabrication methods of particulate reinforced aluminium metal matrix composite – A review. *Mater. Today Proc.* 5, 5933–5939.
- Paranthaman, P., Gopal, P.M., Sathiesh Kumar, N., 2019. Characterization of Economical Aluminium MMC Reinforced with Weld Slag Particles, *Lecture Notes in Mechanical Engineering*. Singapore: Springer.

- Prabu, S.B., Karunamoorthy, L., Kathiresan, S., Mohan, B., 2006. Influence of stirring speed and stirring time on distribution of particles in cast metal matrix composite. *J. Mater. Process. Technol.* 171, 268–273.
- Pradeep Kumar, J., Robinson Smart, D.S., Selvan, C.P., 2018. Experimental evaluation of strength and wear rate of AA7075/TAC/Si₃N₄/Ti nano hybrid metal matrix composite. *Int. J. Mech. Eng. Technol.* 9, 1690–1698.
- Rahman, M.A., Sirajudeen, N., 2019. Influence of aging, varying particle size & volume fraction of Al₂O₃ particles on the hardness and wear behavior of Al 7150 alloy composite produced by hot uniaxial compaction method. *Mater. Res. Express* 6.
- Raj, R., 2018. Effect of particle size and volume fraction on the strengthening mechanisms of boron carbide reinforced aluminum metal matrix composites. *Proc. IMechE Part C J. Mech. Eng. Sci.* 1–12.
- Rajan, T.P.D., Pillai, R.M., Pai, B.C., Satyanarayana, K.G., Rohatgi, P.K., 2007. Fabrication and characterisation of Al–7Si–0.35Mg/fly ash metal matrix composites processed by different stir casting routes. *Compos. Sci. Technol.* 67, 3369–3377.
- Ramachandra, M., Radhakrishna, K., 2007. Effect of reinforcement of fly ash on sliding wear, slurry erosive wear and corrosive behavior of aluminium matrix composite. *Wear* 262, 1450–1462.
- Ramakoteswara, V., Ramanaiah, N., Moulana, M., Sarcar, M., 2016. Mechanical and tribological properties of AA7075–TiC metal matrix composites under heat treated (T6) and cast conditions. *Integr. Med. Res.* 5, 377–383.
- Ramesh, B.T., Swamy, R.P., Vinayak, K., 2018. Mechanical characterization of Al-2024 reinforced with fly ash and E-glass by stir casting method. *AIP Conf. Proc.* 1943.
- Rammath, B.V., Elanchezian, C., Atreya, T.S.A., Vignesh, V., 2014. Aluminum metal matrix composites – A review. *Rev. Adv. Mater. Sci.* 38, 55–60.
- Rana, R.S., Purohit, R., Soni, V.K., Das, S., 2015. Characterization of mechanical properties and microstructure of aluminium alloy–SiC composites. *Mater. Today Proc.* 2, 1149–1156.
- Rao, J.B., Rao, D.V., Catherin, G.J., Bhargava, N.R.M.R., 2011. Development of light weight AA2024 alpha composites. *Mater. Sci. Forum* 690, 258–261.
- Rao, J.B., Rao, D.V., Murthy, I.N., Bhargava, N., 2012. Mechanical properties and corrosion behaviour of fly ash particles reinforced AA2024 composites. *J. Compos. Mater.* 46, 1393–1404.
- Rao, V.R., Ramanaiah, N., Sarcar, M.M.M., 2014. Fabrication and investigation on properties of TiC reinforced Al7075 metal matrix composites. *Appl. Mech. Mater.* 592–594, 349–353.
- Romanova, V.A., Balokhonov, R.R., Schmauder, S., 2009. The influence of the reinforcing particle shape and interface strength on the fracture behavior of a metal matrix composite. *Acta Mater.* 57, 97–107.
- Sahoo, P., Kocak, M.J., 1991. Microstructure-property relationships of in situ reacted TiC/Al–Cu metal matrix composites. *Mater. Sci. Eng.* 131, 69–76.
- Sajjadi, S.A., Ezatpour, H.R., Parizi, M.T., 2012. Comparison of microstructure and mechanical properties of A356 aluminum alloy/Al₂O₃ composites fabricated by stir and compo-casting processes. *Mater. Des.* 34, 106–111.
- Selvaraj, S.K., Nagarajan, M.K., Kumaraswamidhas, L.A., 2017. An investigation of abrasive and erosion behaviour of AA2618 reinforced with Si₃N₄, AlN and ZrB₂ in situ composites by using optimization techniques. *Arch. Civ. Mech. Eng.* 17, 43–54.
- Senthil, P., Amirthagadeswaran, K.S., 2012. Optimization of squeeze casting parameters for non-symmetrical AC2A aluminium alloy castings through Taguchi method. *J. Mech. Sci. Technol.* 26, 1141–1147.
- Sharma, S.S., Pai, A., Gowrishankar, M.C., 2017. Potentiality of artificially aged aluminium 6061 hybrid composites reinforced with granite and graphite micro-fillers for structural applications (Potenzial von künstlich gealterten, mit Granit und Graphit verstärkten Aluminium- (6061) Hybrid-Verbundwerks). *Materwiss. Werkstsch.* 48, 1082–1092.
- Srivatsan, T.S., 1996. Microstructure, tensile properties and fracture behaviour of Al203 particulate-reinforced aluminium alloy metal matrix composites. *J. Mater. Sci.* 31, 1375–1388.
- Srivatsan, T.S., Sudarshant, T.S., Lavernia, E.J., 1995. Processing of discontinuously- reinforced metal matrix composites by rapid solidification. *Prog. Mater. Sci.* 39, 317–409.
- Stjohn, D., Nie, J., 2017. Wrought aluminium alloys. In: *Light Alloys*. Elsevier, pp. 75–80.
- SUPREMEX–Metal Matrix Composites – Lighter, Stiffer, Stronger, 2020. *Materion* (WWW Document). Available at: SUPREMEX–Metal Matrix Composites - Lighter, Stiffer, Stronger (accessed 29 March 2020).
- Tahamtan, S., Halvaei, A., Emami, M., Zabihi, M.S., 2013. Fabrication of Al/A206–Al₂O₃ nano/micro composite by combining ball milling and stir casting technology. *Mater. Des.* 49, 347–359.
- Temponik Test Functional Prototype, 2015. *Light Metal* (WWW document). Available at: <http://www.temponik.com/Material> (accessed 29.03.2020).
- Tesa, 2020. Bonding of Stiffeners and Reinforcement Bars (WWW Document). Available at: <https://www.tesa.com/en/industry/building-industry/applications/bonding-of-stiffeners> (accessed 29.03.2020).
- Tham, L.M., Cheng, L., 2001. Effect of limited matrix-reinforcement interfacial reaction on enhancing the mechanical properties of aluminium-silicon carbide composites. *Acta Mater.* 49, 3243–3253.
- Touchstone, 2020. *Material cOmpression Testing* (WWW document), Touchstone Testing Lab. Available at: <https://www.touchstonetesting.com> (accessed 29.03.2020).
- Ul Haq, M.I., Anand, A., 2018. Dry sliding friction and wear behavior of AA7075–Si₃N₄ composite. *Silicon* 10, 1819–1829.
- Umunakwe, I.J., 2017. Effects of stirring time and particles preheating on porosity, mechanical properties and microstructure of periwinkle shell–Aluminium metal matrix composite (PPS–ALMMC). *Int. J. Eng. XV.* 134–140.
- Valibeygloo, N., Azari Khosroshahi, R., Taherzadeh Mousavian, R., 2013. Microstructural and mechanical properties of Al–4.5wt% Cu reinforced with alumina nanoparticles by stir casting method. *Int. J. Miner. Metall. Mater.* 20, 978–985.
- Vijaya Ramnath, B., Jeykrishnan, J., Akilesh, S., Saravanan, B., Krishna Vivek, V., 2018. Investigation of micro-structure and mechanical behaviour of aluminum-zircon sand-tungsten carbide metal matrix composites. *Mater. Today Proc.* 5, 25553–25561.
- Whitehouse, A.F., Clyne, T.W., 1993. Effects of reinforcement content and shape on cavitation and failure in metal matrix composites. *Composites* 24 (3), 256–261.
- Wu, C., Ma, K., Wu, J., *et al.*, 2016. Influence of particle size and spatial distribution of B₄C reinforcement on the microstructure and mechanical behavior of precipitation strengthened Al alloy matrix composites. *Mater. Sci. Eng. A* 675, 421–430.
- Wu, Q., Xu, W., Zhang, L., 2019. Microstructure-based modelling of fracture of particulate reinforced metal matrix composites. *Compos. Part B Eng.* 163, 384–392.
- Yang, H., Jiang, L.I.N., Balog, M., Krizik, P., Schoenung, J.M., 2017. Reinforcement size dependence of load bearing capacity in ultrafine-grained metal matrix composites. *Metall. Mater. Trans. A* 48, 4385–4392.
- Yong, M.S., Clegg, A.J., 2005. Process optimisation for a squeeze cast magnesium alloy metal matrix composite. *J. Mater. Process. Technol.* 168, 262–269.
- Zhang, Y., Topping, T.D., Yang, H., *et al.*, 2015. Micro-strain evolution and toughening mechanisms in a trimodal Al-based metal matrix composite. *Metall. Mater. Trans. A* 46, 1196–1204.
- Zhang, Z., Chen, D.L., 2006. Consideration of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites: A model for predicting their yield strength. *Scr. Mater.* 54, 1321–1326.

Relevant Websites

<https://www.3m.com/>

3M

Advance Materials for Commercial Applications.

<https://map.ethz.ch/research/groups.html>

ETH Zurich Competence Center for Materials and Processes (MaP).

<https://intelligentcomposites.com/>

Intelligent Composites

<https://materion.com/products/metal-matrix-composites/supremex>

Materion.

<https://ntrs.nasa.gov/>

NASA Technical Reports Server.

<http://www.azom.com>

The A to Z of Materials.

<https://sites.uwm.edu/center-for-composites/>

UWM Center for Composites Materials.

Fatigue Behavior of Magnesium Matrix Composites

Sravya Tekumalla, Nanyang Technological University, Singapore

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

In an ever-increasing quest for alternative environment-friendly materials for a sustainable planet, magnesium stands out due to its extremely low density and exceptional property profile such as high specific strength, excellent damping capacity, good machinability, etc. These properties render magnesium alloys useful in automobile applications, such as in low temperature exposure components like covers, engine cases, brackets, etc. (Ramalingam *et al.*, 2020). Demonstration of additional properties such as ignition resistance, low modulus, and electromagnetic shielding extend the applications of magnesium alloys to aerospace, biomedical and electronic sectors, respectively. In the last two decades, there have been numerous publications demonstrating the potential of magnesium composites as an attractive class of magnesium-based materials as they offer better thermal properties such as creep, strength, ignition resistance, electromagnetic shielding resistance, and corrosion. Magnesium matrix composites comprise of pure magnesium or a magnesium alloy as the matrix material with reinforcements such as ceramic/carbon based/amorphous/metallic materials varying in different length scales from micro- to nano-meter scales and hence termed as micro composites and nanocomposites. The effect of different reinforcements on the mechanical properties (i.e., strength and ductility) of magnesium is given in Fig. 1 (Gupta and Wong, 2015). In applications such as biomedicine, materials are subjected to repeated cycles of loading, wherein different human body parts are estimated to undergo different levels of cyclic stresses. For instance, during regular activities, human bones experience stresses up to 4 MPa while ligaments and tendons are subjected to peak stresses ranging from 40 to 80 MPa. Likewise, hip joints usually witness 3–10 times the weight of the body during activities like jumping. These stresses occur in the form of irregular repetitive cycles of loading and are estimated to reach up to 10^6 cycles/year. In order to serve as a potential replacement material/implant material, magnesium matrix composites need to withstand these conditions and demonstrate a good fatigue resistance. In materials science, the term “fatigue”, by definition, is the weakness in a material caused due to a repeated variation in stresses. According to the American Society of Testing and Materials (ASTM) (ASTM, 2013), fatigue is defined as “the process of progressive localized permanent structural change occurring in a material subjected to conditions that produce fluctuating stresses and strains at some point or points and that may culminate in cracks or complete fracture after a sufficient number of fluctuations”. Since failure by fatigue can occur despite the generated stress being lower than the yield point, it becomes imperative to study the conditions of fatigue crack growth to understand the fatigue lifecycle of the materials. Particularly, foreign reinforcements in otherwise homogenous magnesium matrix act as stress concentration and potential crack initiation sites promoting fatigue failure.

Depending on the origin of the stresses in materials, fatigue is classified into several types such as (1) Mechanical fatigue, (2) Thermal fatigue, and (3) Corrosion fatigue. Mechanical fatigue, the most commonly observed fatigue in metals, is a result of exposure to cyclic mechanical stresses for an extended period of time. Examples of fatigue failure include the 1954 De Havilland Comets airline crashes where the passenger jets had broken up in mid-air due to the presence of sharp corners in the window openings of the planes. These sharp corners acted as stress concentration sites that initiated cracks. Repeated stress cycles in the fuselage were generated from pressurization and depressurization of the aircraft during each flight which led to propagation of cracks over time. After a finite number of cycles, the crack reached a threshold/critical length that prompted fuselage shell failure. Thermal fatigue is a specific type of fatigue failure mechanism marked by the slow deterioration and subsequent cracking of a material subjected to alternate heating and cooling cycles during which the material's free thermal expansion/contraction is constrained partially or fully. Thermal fatigue may/may not occur with mechanical loads. The degree of damage is affected by the magnitude and frequency of the temperature swings. Historically, it is known to be one of the major reliability threats in structural applications (Bayani and Saebnoori, 2009). Corrosion fatigue is the degradation of a material subjected to simultaneous action of cyclic loading and corrosive environments. A routine feature of corrosion fatigue is the corrosion pits which lead to crack initiation and propagation in parts subjected to cyclic loads (van der Walde *et al.*, 2005), and therefore, corrosion pits that reach a critical size have detrimental effects on fatigue life of a component. Fig. 2(a) and (b) gives a typical example of corrosion fatigue failure.

While all the three phenomena do occur in magnesium matrix composites, this article broadly covers the mechanical fatigue of magnesium matrix composites unless stated otherwise. Despite the limited work done by the scientific community in the thermal and corrosion fatigue of composites, this article also highlights the potential research directions pertaining to those topics.

Mechanical Fatigue of Magnesium Matrix Composites

Mechanism of Deformation and Failure in Magnesium

With a hexagonal closed-packed (HCP) lattice structure and a c/a ratio of 1.624, magnesium does not obey the von Mises criterion to have five independent active slip systems for homogeneous deformation. Therefore, the ductility of the material is limited as it does not sustain a large amount of plastic deformation by slip. Instead, magnesium undergoes deformation by

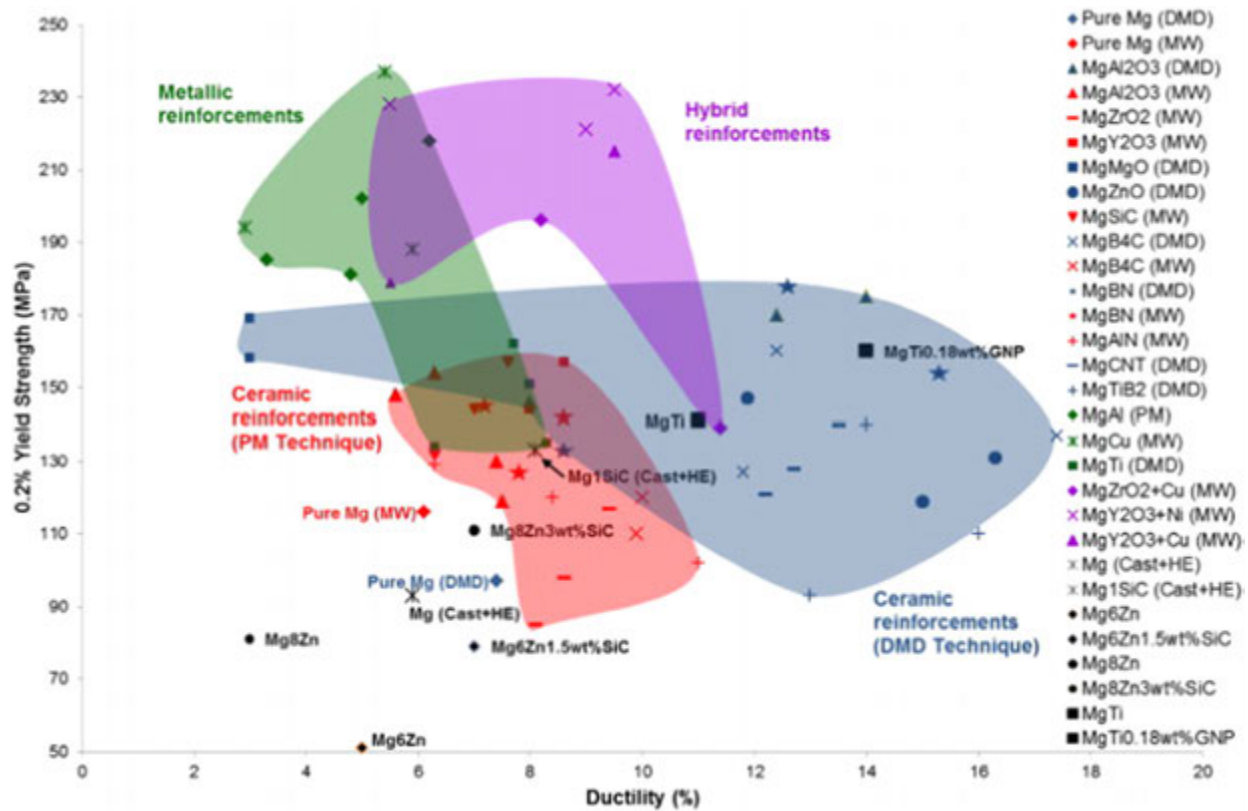


Fig. 1 Schematic illustrating the role of particulate reinforcements on tensile properties of magnesium matrix. Image reproduced from Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.

both slip and twinning based mechanisms. Among various deformation modes (Albinmousa, 2020), the basal (0001) slip and the (10 $\bar{1}2$) tension twinning are the easy modes of activation owing to their low critical resolved shear stresses (CRSS). In cyclic loading, especially involving tension-compression cycles, apart from slip, a twinning-detwinning deformation mode is experienced by magnesium alloys and composites (particularly, wrought). This is because of a tension-compression asymmetry experienced by the materials which results in a stress asymmetry leading to a high mean stress. This article presents different aspects of fatigue of magnesium matrix composites, including the role of micron, sub-micron, and nano reinforcements on the fatigue life, followed by the microstructural aspects of the composites. For more information on the general concepts of fatigue including experimental methods, fatigue life equations and damage models, the readers are redirected to the article by Albinmousa (2020).

Fatigue of Magnesium Matrix Composites

Micron size reinforcements

Amorphous reinforcements

Amorphous alloys are a class of metallic materials that are not crystalline in nature as compared to most metals, but demonstrate great properties such as high strengths (in the order of 1–2 GPa), high elastic strain limits of up to 2%, good corrosion resistance, etc., (Inoue, 1995). Given the unique nature of amorphous alloys, researchers have used these amorphous materials as reinforcements for making lightweight metal matrix composites. Nafar Dastgerdi *et al.* (2016) reinforced micron sized amorphous alloy particles of composition Ni₆₀Nb₄₀ (by at%) via blending different fractions (3% and 5% by volume) of it with Mg powder, followed by compaction, sintering and extrusion. They conducted fatigue loading at $R = -1$, frequency = 20 Hz at room temperature and reported that the specimen with uniform distribution of particle possessed superior fatigue resistance and higher fatigue limit. Further, they demonstrate higher fatigue life of composites reinforced with amorphous particulates as compared to pure Mg in high cycle region as given in Fig. 3. As one would expect, the fatigue crack initiation occurred preferentially at particle-matrix interfaces with multiple cracks initiated at the interface between the Ni₆₀Nb₄₀ particles and the matrix. These small cracks tended to propagate without interacting with other cracks. However, with time, these multiple cracks coalesce with one another to propagate and grow. Therefore, the fatigue behavior of the composites with amorphous particulates is strongly interlinked with the particulate distribution in the microstructure which, of course is a derivative of the processing conditions. In non-uniformly

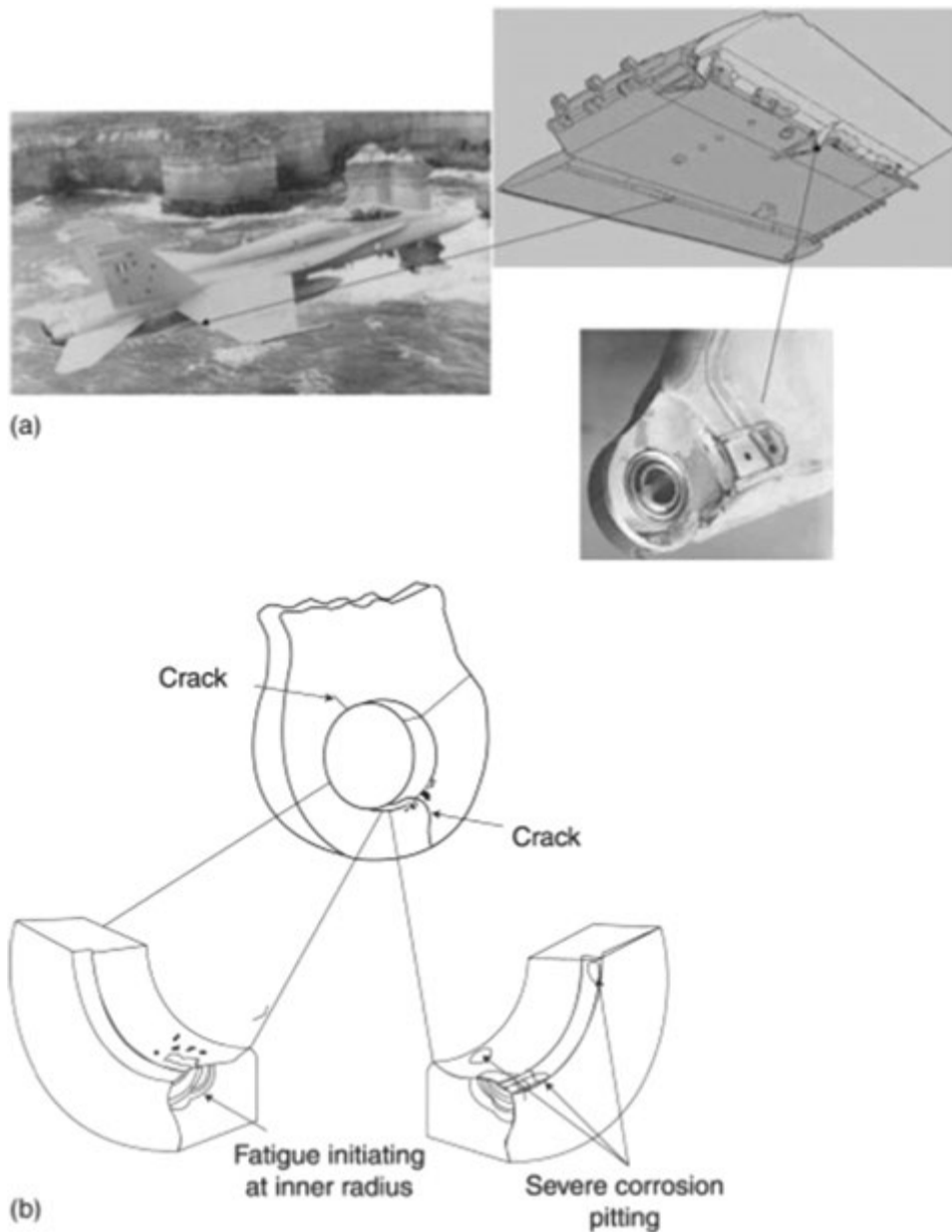


Fig. 2 (a) A F-18 aircraft wing trailing edge flap undergoing corrosion fatigue failure; (b) Micro-section of region that underwent fatigue cracking.

distributed microstructures, several cracks coalesce together, while microstructures with uniform particle distribution witness, fewer fatigue crack coalescence, therefore delaying the fatigue failure.

Fibers

Alumina fibers

Nunes *et al.* (1986) studied ZE41 magnesium matrix with different volume fractions of alumina fibers (35, 40, 45, 55 vol%) with $R = 0.1$ under controlled loads at room temperature. Since the alumina fibers are much stronger than the magnesium matrix, they can take far superior loads when the composite is loaded. Hence, the tensile and fatigue deformation of the ZE41A/FP composites is controlled by the fracture of the fibers, with the final fracture occurring when enough fibers were fractured and congregated at a particular region. The authors also note the change in the mechanical properties with a change in orientation of the fibers, however, at any given orientation, the composite always demonstrated superior mechanical properties as compared to the base alloy (up to 40% higher), which demonstrates the positive effects of reinforcement on the mechanical properties such as tensile and fatigue as given in Fig. 4 for ZE41 with 55% FP composite. Further, apart from the reinforcement, the authors also highlight

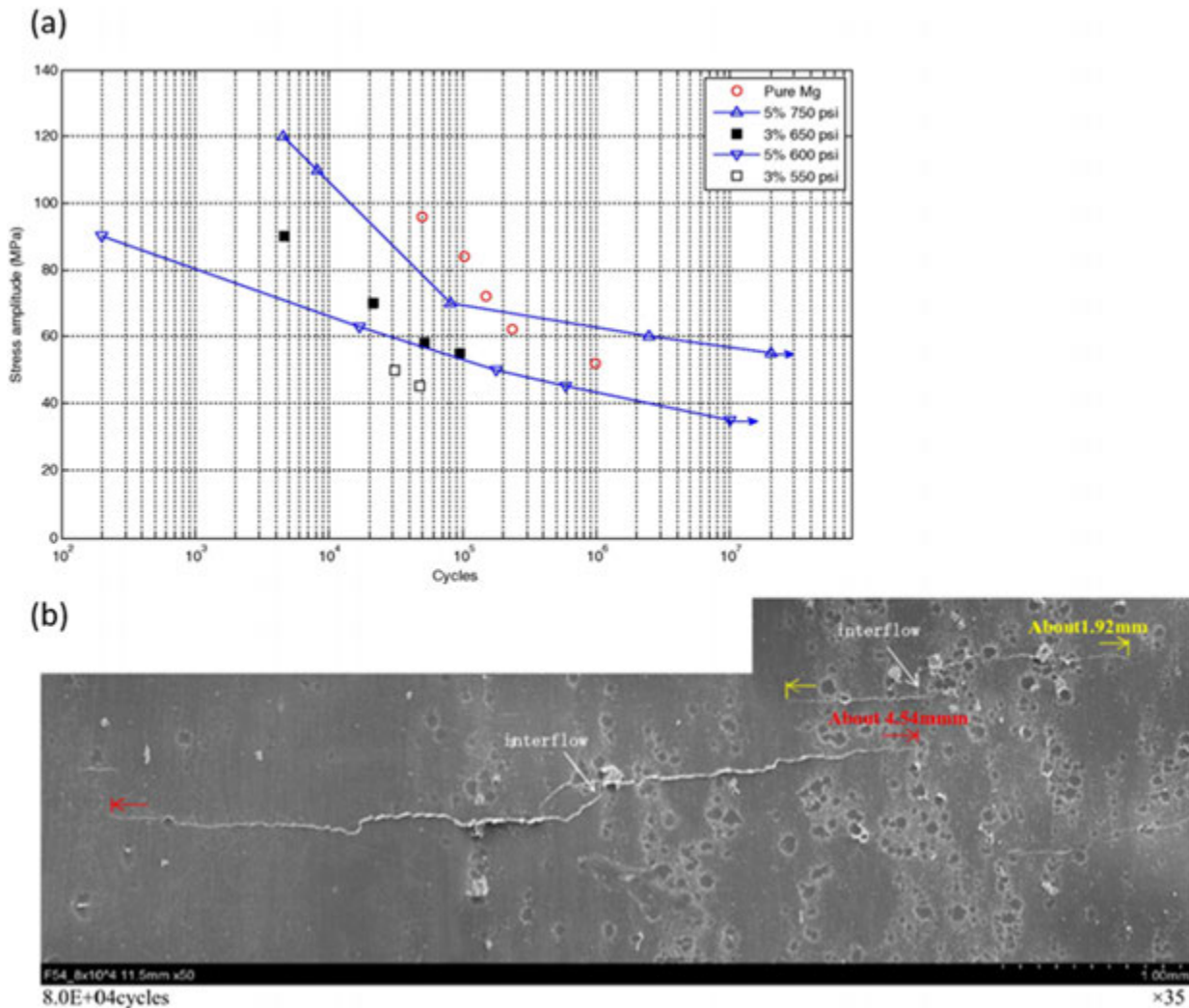


Fig. 3 (a) S–N curves of Mg/Ni₆₀Nb₄₀ amorphous particles reinforced composites; (b) Cracks initiation and propagation of Mg/5Ni₆₀Nb₄₀ composite.

the importance of matrix alloy chemistry on the final mechanical properties. A matrix with double zinc and five times zirconium content exhibited significantly higher tensile and fatigue properties.

In a similar study, Davidson *et al.* (1989) reported the retardation of the crack growth rates by the fibers in the composite. In materials having fibers oriented at 0° to the loading axis, the fracture of fibers ahead of the crack tip, followed by coalescence of the cracks with the main crack was the predominant mode of crack growth. When the fracture strength exceeded in the crack tip region, fracture of fibers was seen to occur, however no debonding of fibers from matrix was observed. However, when the orientation of the fibers was changed from 0° to 45° , cracks were noticed adjacent to interfaces and the fracture was mainly due to the interface debonding. Tevatia and Srivastava (2015) proposed an analytical model based on the modified shear lag (MSL) theory which better agrees with the fatigue crack growth life for both low cycle and high cycle fatigue applications. Although validated by experiments on aluminum based short fiber MMC under the total strain-controlled settings, the authors propose the validity of the model for all metal matrix composites which proposes: a higher amplitude of plastic strain amplitude, a higher fiber volume fraction, and a high cyclic strain hardening exponent and low cyclic strength coefficient lead to an increased fatigue crack growth life.

Carbon fibers

Carbon fibers were also studied as reinforcement to a AZ91 magnesium alloy matrix by. Qi *et al.* (2017) and focus was laid on understanding the fatigue behavior of the composites. Load-controlled tests were performed with the $R = 0.1$ at a frequency of 15 Hz, hence it must be noted that there was no introduction of compressive stresses. It was estimated that the fatigue limit of the Mg/Cf composites was 250–270 MPa i.e., about 65%–70% of their ultimate tensile strength (~ 385 MPa). These composites showed high fatigue resistance did not fail at loads where cycles exceeded 10^4 demonstrating a reinforced fatigue behavior. Like alumina

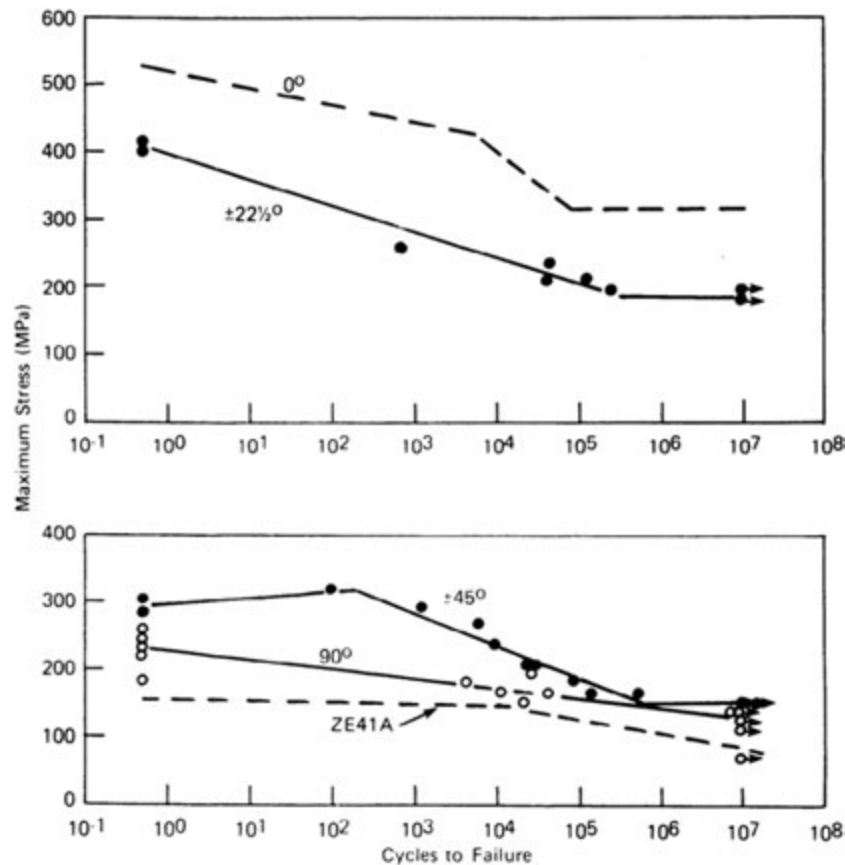


Fig. 4 Fatigue of ZE41/FP composite and ZE41A magnesium alloy at a test temperature of 24°C and a constant fiber volume fraction of 55%. Reproduced from Nunes, J., Chin, E.S., Slepetz, J.M., Tsangarakis, N., 1986. Tensile and fatigue behavior of alumina fiber reinforced magnesium composites. *Metallurgical Transactions A* 15, 1397–1405.

fibers, the carbon fibers also show “interface weakening effect” with the matrix due to the debonding of the fibers with the matrix which eventually results in pull-outs of fibers and numerous cracks as shown in Fig. 5. As the applied max. load/cycles increases, there is an increased fiber pull-out and cracks cycles leading to “interface weakening effect” which is detrimental to the fatigue behavior.

Spherical reinforcements

Micron size spherical reinforcements such as SiC particulates have been added to Mg-6Zn alloy to study the mechanical properties including cyclic fatigue behavior. Llorca (1994) studied the micro composite in T4 and T6 conditions and noted that hysteresis loops shape of the composite in T4 condition is symmetrical (Fig. 6(a)) with compressive stresses consistently lower than the tensile stresses by 50 MPa upon fatigue loading. This is due to the tension-compression yield asymmetry displayed by magnesium alloys owing to their crystal structure. However, the authors report that the magnesium based composites were not as sensitive to cyclic loading as compared to aluminum based composites. In fact, the naturally aged magnesium composite demonstrated cyclic hardening while the artificially aged T6 composite did not due to the presence of Mg-Zn phase. Hence, the influence of secondary phases, apart from reinforcements, is critical in dictating the fatigue life of the composite. In another work on the same materials, Srivatsan *et al.* (2005) studied the fatigue at room temperature and elevated temperature (150°C) (Fig. 6(c)). The authors observed agglomeration of particles in the microstructure owing to the size of the particles and presence of weak Van der waal’s forces that exist between the particulates. Crack initiation was favored at low stresses because of the presence of hard and brittle SiC particles in relatively ductile and soft magnesium alloy matrix. At 150°C, the addition of particles showed an increased fatigue resistance (based on normalizing the cyclic stress amplitude with yield strength). Overall, because of constraints due to the hard and brittle SiC particles in the matrix led to the formation of stress concentration sites locally at the interface of matrix and reinforcement promoting fatigue failure in the matrix. The mode of fracture is through the crack initiation and growth in the interfaces and coalescence of voids.

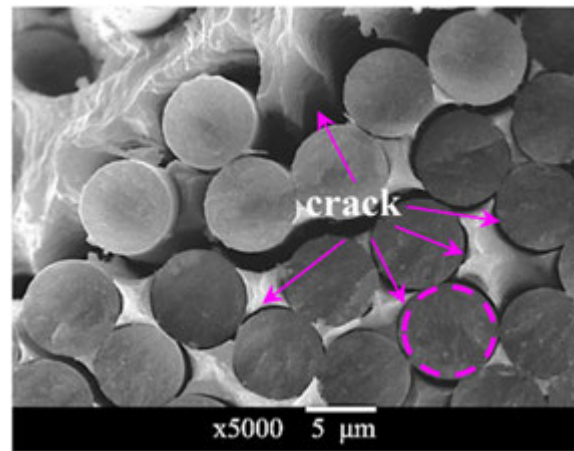


Fig. 5 Microfracture of fatigued Mg/Cf composite.

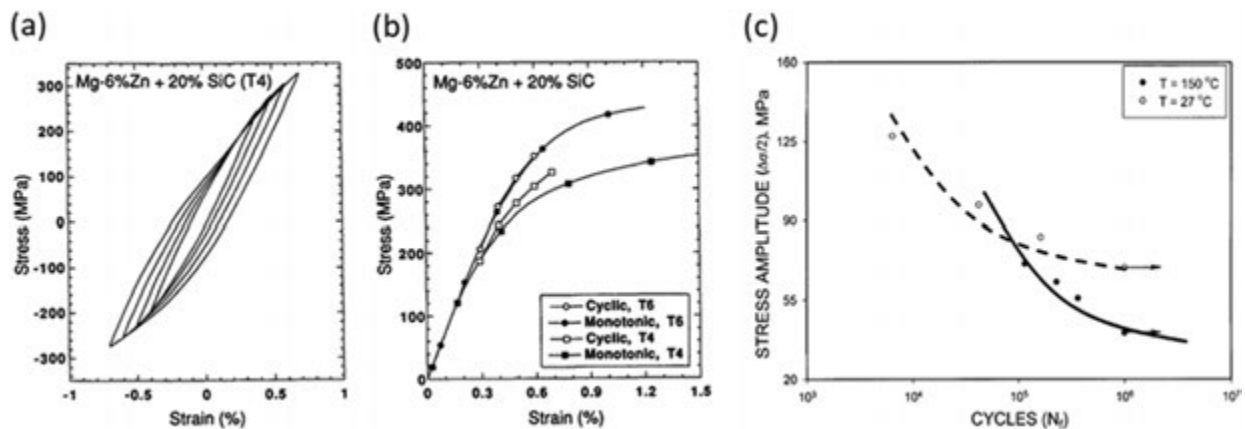


Fig. 6 (a) Hysteresis loops for Mg-6Zn/20SiC composite; (b) Tensile and cyclic stress-strain curves for the Mg-6Zn/20SiC composite; (c) SN curves at room temperature and 150°C for Mg-6Zn/20SiC composite.

Sub-micron reinforcements

For biomedical applications, [Sabet *et al.* \(2018\)](#) developed Mg/2.5 wt% HA (Hydroxyapatite) and Mg/5 wt% HA bio-composites (average particle size ~ 600 nm). High cycle fatigue tests on these composites showed superior behavior of the composites over pure Mg ([Fig. 7](#)) with $> 10^7$ cycles life. Mg/2.5HA performed better as compared to Mg/5HA composite at all stress amplitudes because of the improved strength of the materials with the reinforcements. The authors propose that the reinforcements helped in redirecting the crack propagation leading to fatigue life enhancement. Further, the authors also propose the possibility of agglomeration of HA particles which led to crack initiation in the composites.

Nano-size reinforcements

Ex-situ added nanoparticles

Ex-situ synthesis refers to the synthesis of the nanocomposites externally without the involvement of any unanticipated/unprecedented chemical reactions. Several nanoparticles such as Al_2O_3 , CNTs have been added to AZ31 magnesium alloy to study the role of nanoparticles on fatigue behavior. Based on a fatigue study of AZ31 alloy + Al_2O_3 nano-reinforcement ([Srivatsan *et al.*, 2013](#)) at room temperature, the nanocomposite displayed a delayed crack initiation and propagation as compared to the monolithic AZ31 alloy, and therefore a higher endurance limit (at 10^6 cycles) as given in [Fig. 8\(a\)](#). Further, the overload region in the nanocomposite showed a high density of dimples apart from microscopic voids, while the AZ31 alloy displayed striations indicating varying modes of deformation in the alloy and the nanocomposite. At elevated temperatures of 100°C, [Jabbari *et al.* \(2020\)](#) demonstrated that the effect of reinforcing particles becomes more significant on the fatigue strength and life of the nanocomposite. The nanocomposites underwent higher cycles of loading as compared to the monolithic alloy at all amplitudes. Additionally, at 100°C the nanoparticles enhanced the fatigue strength by 87%, and by 50% at 200°C. The improvement was

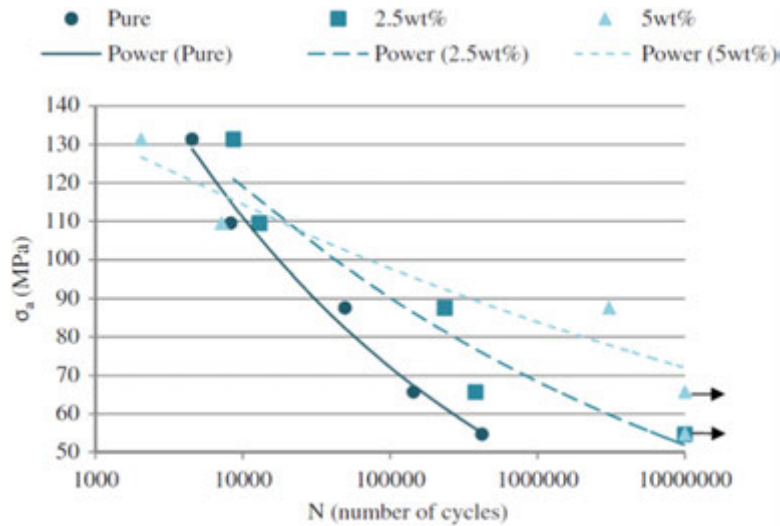


Fig. 7 SN curves of pure Mg, Mg/2.5HA and Mg/5HA at room temperature.

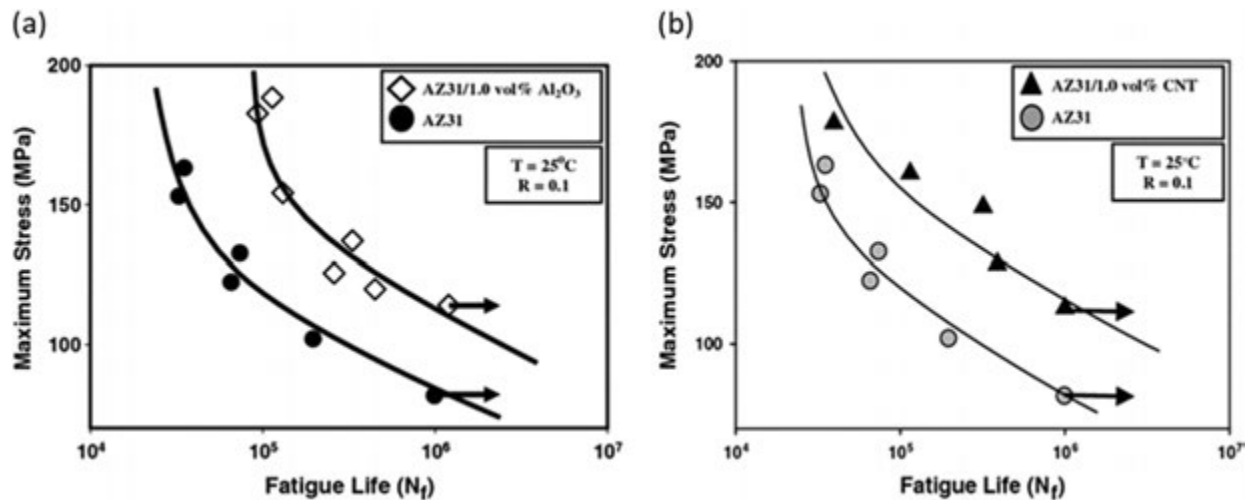


Fig. 8 Maximum stress vs. fatigue life at $R = 0.1$ of (a) AZ31 and AZ31/1Al₂O₃ nanocomposite; and (b) AZ31 and AZ31/1CNT nanocomposite. Reproduced from Srivatsan, T.S., Godbole, C., Quick, T., Paramsothy, M., Gupta, M., 2013. Mechanical behavior of a magnesium alloy nanocomposite under conditions of static tension and dynamic fatigue. *Journal of Materials Engineering and Performance* 22 (2), 439–453. Srivatsan, T.S., Godbole, C., Paramsothy, M., Gupta, M., 2012a. Influence of nano-sized carbon nanotube reinforcements on tensile deformation, cyclic fatigue, and final fracture behavior of a magnesium alloy. *Journal of Materials Science* 47 (8), 3621–3638.

attributed to the improvement in the tensile strengths of the nanocomposites at higher temperatures, especially at 200°C, owing to the presence of thermally stable nanoparticles which led to a desirable high cycle fatigue behavior in the nanocomposites at higher temperatures. This led to a delayed crack initiation, propagation, and growth, thereby improving the fatigue performance. Moreover, the nano particles have also been deemed to deflect or hinder the fatigue crack growth paths by acting as obstacles to the cracks.

With addition of nanoparticle-sized CNT reinforcements (Srivatsan *et al.*, 2012a), the AZ31/1CNT (vol%) composite also had an endurance limit that is 40% higher than AZ31 alloy (at $R = 0.1$ and $R = -1$). Therefore, the AZ31/CNT nanocomposites are deemed favorable from a cyclic fatigue standpoint as shown in Fig. 8(b). An improvement by 200% was observed in the HCF life with addition of CNT nanoparticles as reinforcement to AZ31 matrix. Therefore, it is proposed that addition of nanoparticles is regarded as the best option to increase the fatigue resistance of the magnesium matrix among all other reinforcements.

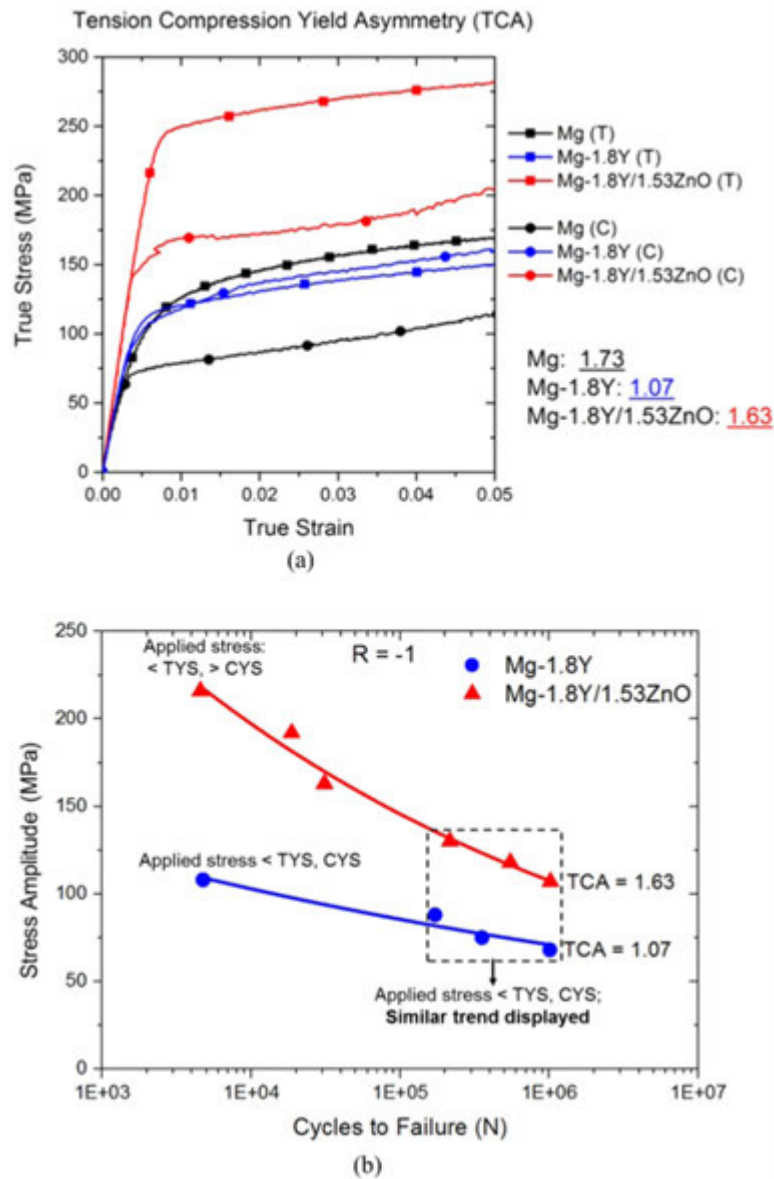


Fig. 9 (a) True stress strain curves of pure Mg, Mg-1.8Y and Mg-1.8Y/1.53ZnO nanocomposite with tension compression asymmetry values, (b) S-N curve of the alloy and nanocomposite ($R = -1$). Image reproduced from Tekumalla, S., Bibhanshu, N., Shabadi, R., *et al.*, 2018. Evolution of texture and asymmetry and its impact on the fatigue behaviour of an in-situ magnesium nanocomposite. Materials Science and Engineering: A 727, 61–69.

In-situ formed nanoparticles

In-situ synthesis typically refers to the “synthesis due to a chemical reaction in the reaction mixture”. This may be done because the species is unstable, and cannot be isolated, or simply out of convenience. It is known that nanoparticles, owing to their large surface energies/Van der Waals force between each other, tend to agglomerate in molten metal. Previous works demonstrated the formation of micro-clusters by ceramic nanoparticles which consequently segregate after ultrasonic processing stops (Min *et al.*, 2008). Recently, it is shown that the in-situ formation of nanoparticles reduces the tendency for agglomeration and therefore, generates a microstructure with uniformly dispersed nanoparticles (Tekumalla *et al.*, 2017). The prime advantage with the in-situ nanocomposites/in-situ evolution of nanoparticles is the feasibility of uniformly distributed nanoparticles in the matrix contrary to ex-situ composites. This helps in arresting the premature failure of the material. Hence, understanding the role of microstructure and in-situ reactions on the final fatigue behavior is critical. Tekumalla *et al.* (2018) studied the role of in-situ reactions on microstructure and mechanical behavior and reported the role of microstructure on tension compression asymmetry which in turn affects the fatigue properties of the in-situ nanocomposite compared to the matrix alloy. As shown in Fig. 9, the fatigue behavior of the in-situ nanocomposite is seen to be much better in contrast to Mg-1.8Y alloy. Further, the authors also correlate the SN curve

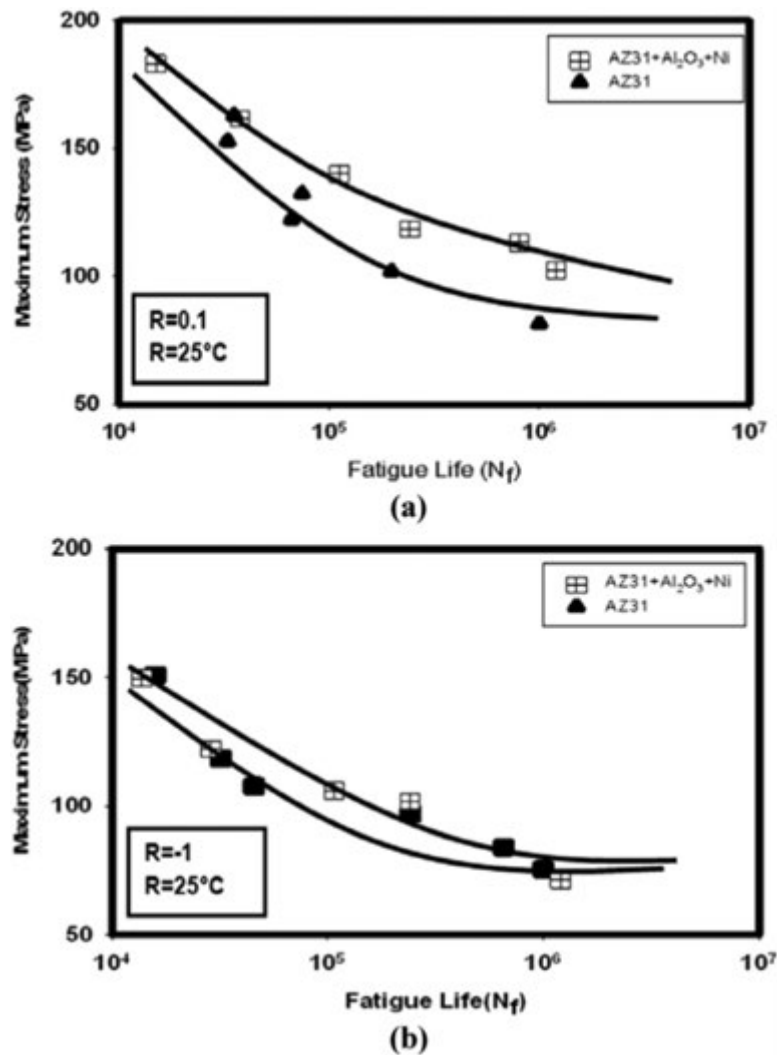


Fig. 10 Maximum stress vs. fatigue life of the AZ31 + Al₂O₃ + Ni hybrid composite at (a) $R = 0.1$ and (b) $R = -1.0$.

slope with tension compression asymmetry of the alloy and nanocomposite and conclude that a high TCA is an indicative of a steeper SN curve.

Hybrid reinforcements

Another approach of using a hybrid mix of reinforcements is sought to achieve materials with properties that cannot be achieved with one type of reinforcement exclusively. With this outlook, nano length scale aluminum oxide (Al₂O₃) particles were added together with micron sized Ni particles as reinforcements to AZ31 to form AZ31/1.5Al₂O₃ + 1.5Ni (vol%). [Srivatsan et al. \(2012b\)](#) reported superior fatigue life and fatigue limit for the magnesium alloy reinforced with the dual-particles by 50%–100%. The maximum stress vs fatigue life at $R = 0.1$ and -1.0 for the alloy and dual particle reinforced composite are shown in [Fig. 10](#). This suggests the beneficial role of the particles in delaying the crack initiation and therefore improving the cyclic fatigue resistance of the matrix.

Based on the micro, nano and hybrid reinforcements, it can be affirmed that the reinforcements addition, particularly nano-sized particles, assists in improving the fatigue life of magnesium significantly.

Microstructural Influence on Mechanical Fatigue Behavior

As can be seen from the section “Mechanical Fatigue of Magnesium Matrix Composites”, it is evident that the reinforcements have a significant effect on the magnesium matrix to achieve improved fatigue life. However, it must be noted that this increased fatigue life is ultimately dependent on the microstructure change brought out in the material due to the addition of the reinforcements. The different factors that influence the fatigue strength and endurance limit are detailed below:

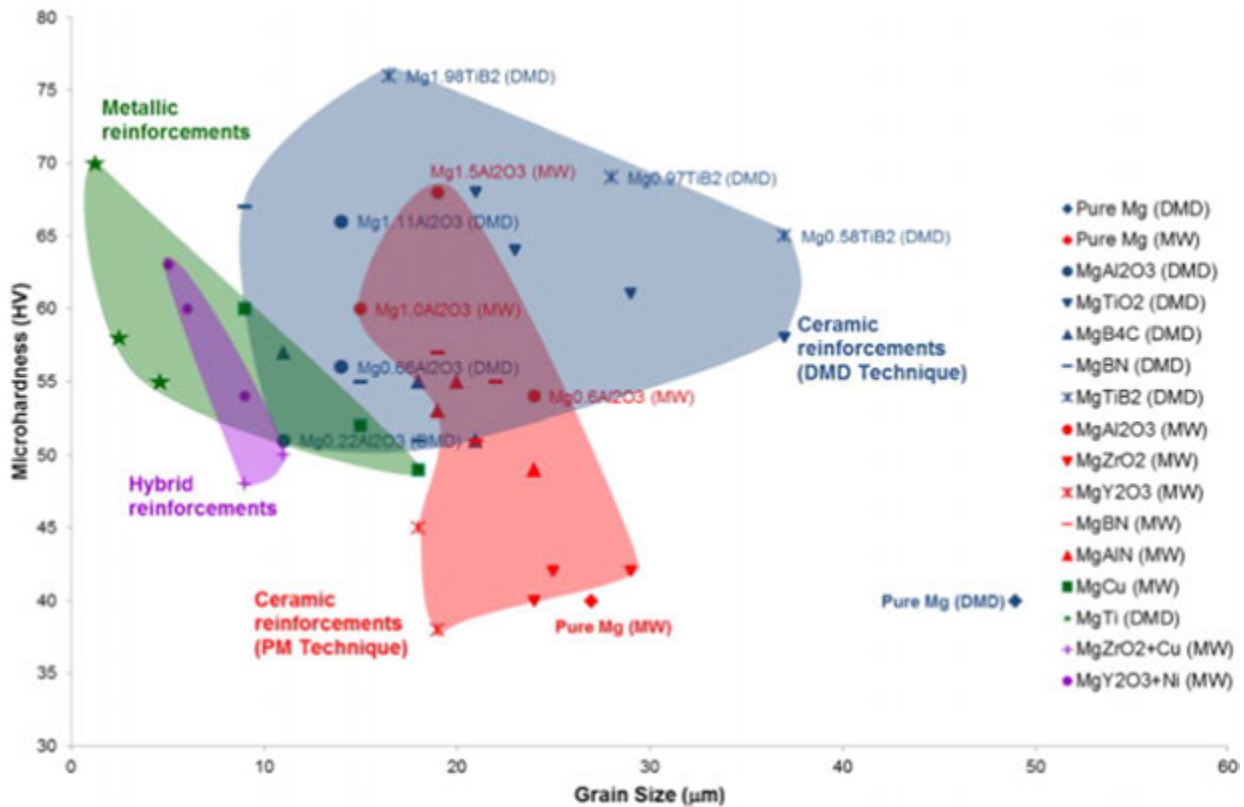


Fig. 11 Grain size changes in magnesium nanocomposites with the addition of reinforcements. Image reproduced from Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.

Defects

Mayencourt and Schaller (2002) demonstrated that the presence of defects such as impurities, interfacial reactions and dislocations are detrimental for the fatigue performance of the composites. In case of Mg-2Si/Al₂O₃ composites, poor damping capacity, relaxation of mechanical stresses by accumulation of damage, and poor fatigue resistance was observed due to the presence of impurities in the matrix, which were a result of interfacial reactions. On the other hand, Mg-2Si/C composite demonstrate excellent mechanical fatigue resistance and damping capacity owing to the lower number of defects. In magnesium-based materials, mechanical stress relaxation relates to dislocation pinning–depinning friction mechanism from point defects, very similar to thermal stress relaxation. When the dislocation is free to vibrate, this mechanism is predominant and therefore promotes crack propagation.

Grain Size

It is generally observed that the addition of reinforcement like HA, CNT, Al₂O₃, and other particles decreases the average grain sizes of the Mg matrix significantly. Fig. 11 gives a complete overview of general decrease in average grain size of micro- and nano-composites in contrast to pure Mg. The most proposed reasons for grain refinement are synergistic influence of pinning effect of the particles and dynamic recrystallization (DRX) made possible during the casting and secondary processing such as hot extrusion (Srivatsan *et al.*, 2013). Jabbari *et al.* (2020) reported a 58% reduction in the grain size of the AZ31B/1.5Al₂O₃ (vol%) composite in contrast to AZ31 monolithic alloy. Following the Hall petch relationship, decreased grain size leads to increased strengths of the material therefore promoting fatigue strength of the materials significantly. Further, reduction in the grain size is one of the only strengthening mechanisms that also contributes to improved ductility. This also helps in improving the endurance limit of the materials.

Texture

Magnesium, typically, exhibits a strong crystallographic texture which strongly influences its mechanical deformation behavior. Different reinforcements influence the crystallographic texture differently (Tekumalla *et al.*, 2019) with certain nano reinforcements like ZnO and Y₂O₃ to pure magnesium matrix weakening the texture. It has been reported that an in-situ Mg-1.8Y/1.53ZnO

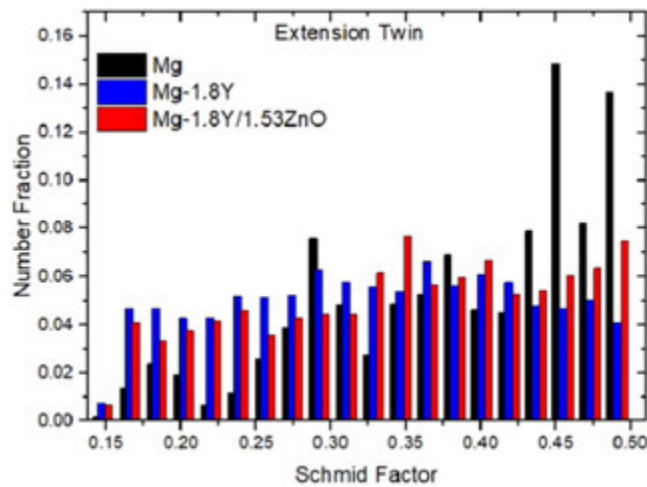


Fig. 12 Number fraction of extension twins in extruded Mg alloys and nanocomposite. Image reproduced from Tekumalla, S., Bibhanshu, N., Shabadi, R., *et al.*, 2018. Evolution of texture and asymmetry and its impact on the fatigue behaviour of an in-situ magnesium nanocomposite. *Materials Science and Engineering: A* 727, 61–69.

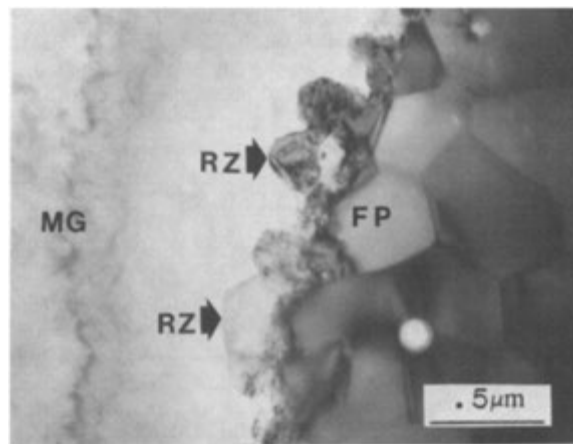


Fig. 13 TEM image of the zone showing magnesium matrix and fiber reaction in ZE41A. Reproduced from Page, R.A., Hack, J.E., Sherman, R., Leverant, G.R., 1984. Tensile and fatigue behavior of aluminum oxide fiber reinforced magnesium composites: Part II. Alloying effects. *Metallurgical Transactions A* 15 (7), 1397–1405.

nanocomposite exhibits a strong two component texture (basal and prismatic) which led to a high tension compression asymmetry (TCA) of 1.63 in comparison to the near symmetric TCA (~ 1.07) in monolithic Mg-1.8Y alloy. Under compressive loading, extension twinning is favored in strongly textured materials such as the nanocomposite as given in Fig. 12, whereas the twinning is suppressed by the weakly textured materials. The activation of twinning in the nanocomposite under compression resulted in the pronounced TCA as slip governed the tensile deformation and twinning governed the compressive deformation. However, the fatigue strength is far superior to the alloy because of the strengthening due to the addition of nano-reinforcements.

Reinforcement (Size, Distribution, Orientation, Stability)

The distribution, size, reactivity, and orientation of reinforcement are all highly localized factors that affect the crack initiation and growth in particle reinforced magnesium matrix, especially in the vicinity of the crack tip. For instance, crack growth rate through an agglomerated region is much higher than the growth rate through a region of well-distributed particles or through the matrix. From the above sections, it is also evident that the smaller the size of reinforcement (i.e., nano scale) the higher the fatigue life and fatigue strength.

Reaction between reinforcement and matrix occurs because of prevailing thermodynamic rules and in the case of fibers in ZE41A matrix, for example, there occurs a loss in fatigue strength of the composite (by 19%) (Page *et al.*, 1984). The interfacial reaction zone (0.25 μm in width) is given in Fig. 13 where the location of interfacial reaction acts as crack initiation site. Due to the reaction of the fibers, there is also an accompanied decrease in the strength of the overall fibers by 20%. Further, because of the

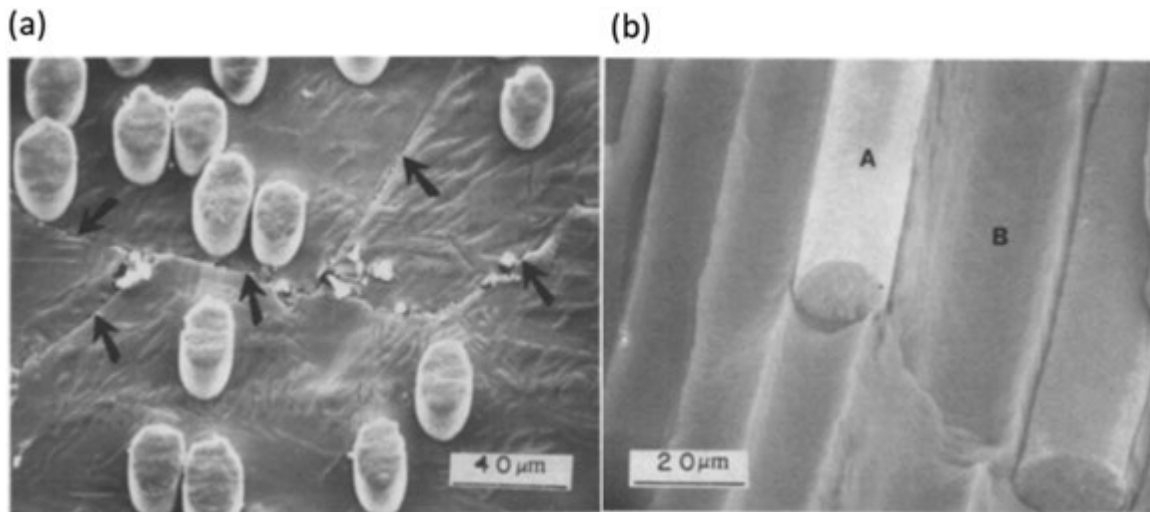


Fig. 14 SEM image of a secondary crack located in the matrix of an off-axis fatigue specimen of Mg/Al₂O₃ fiber composite. Note that the cracking avoids fiber/matrix interfaces during subcritical crack growth (crack path denoted by arrows). (b) SEM image of the failure obtained in the scanning Auger microprobe. Reproduced from Hack, J.E., Page, R.A., Leverant, G.R., 1984. Tensile and fatigue behavior of aluminum oxide fiber reinforced magnesium composites: Part I. Fiber fraction and orientation. *Metallurgical Transactions A* 15 (7), 1389.

formation of a layer initially formed during solidification followed by the reaction/fusion zone of the fibers and matrix, the zone consists of strains from differential contraction which results in the generation of dislocations.

It is also commonly proposed that the fatigue deformation of magnesium matrix composites is a function of the orientation of reinforcements, particularly, fibers. In one study, magnesium was reinforced with 20-micron average diameter Al₂O₃ fibers (35 vol % and 55 vol%) such that the fibers were laid out in a unidirectional fashion (Fig. 14). With the resultant material having extremely large grains (spanning through thickness), the microstructure was similar for both the composites. Increasing the angle between fiber axis and the stress axis resulted in a reduction in the fatigue resistance (Fig. 15(a)). Further, the material with higher fiber volume fraction demonstrated higher increase in the fatigue resistance for the axial samples. Further, the data presented in Fig. 15(b) also indicates that fatigue resistance scales roughly with the UTS (0.6%–0.95% UTS). Generally, it was observed that the fatigue failure happened with cracking occurring across the fibers at roughly 90 degrees to their axial direction. The authors attribute the failure to process defects such as (1) breaking and falling of individual fibers perpendicular to the stress axis during processing and (2) clumping of Al₂O₃ fibers such that their size is an order of magnitude larger than the grain diameter. These led to the delamination of the fibers from the magnesium matrix. However, these process defects did not play a significant role in the crack initiation during off-axis loading. Fatigue crack initiation and propagation during off-axis loading occurred primarily through magnesium matrix. Hence, matrices with better strengths obtained through modification of alloy chemistry are recommended for increasing the off-axis fatigue resistance of the composites.

Thermal Fatigue of Magnesium Matrix Composites

Since magnesium matrix has a mismatch in coefficient of thermal expansion/contraction with its various ceramic, carbon-based, other metallic reinforcements, large thermal stresses can be introduced in the magnesium composites with any change in the environmental temperature. This can potentially result in localized deformation (both elastic and plastic) at the matrix-reinforcement interface. This leads to dimensional instability of the structure resulting in degradation of mechanical properties, also termed as *thermal fatigue*. With increased dislocation density near the matrix-reinforcement interface, there is a chance that ageing and consequently, over-ageing of the matrix can be accelerated. Huang *et al.* (2006) worked on the thermal fatigue deformation of magnesium alloy composites (AE42 alloy with short Al₂O₃ fibers, transverse and longitudinal) as shown in Fig. 16. The authors suggest that the residual strains in the materials developed as a result of thermal cycles are dependent on the heat treatment, fiber composition and fiber orientation (in magnesium matrix). The residual strain is seen to increase with thermal cycles in longitudinal sample, while decrease in the transverse samples. Further, the samples with T6 treatment that underwent ageing, was seen to have the lowest residual strains. This is ascertained to be because of the increase in the yield strength of the matrix with ageing treatment. The authors note that the thermal stresses are released through plastic deformation of the magnesium matrix under thermal cycling. These thermal cycles result in the degradation of properties via phenomena like matrix overaging and recovery. Therefore, a thorough understanding of the thermal fatigue failure phenomenon is essential in design of magnesium matrix composites for use in such conditions.

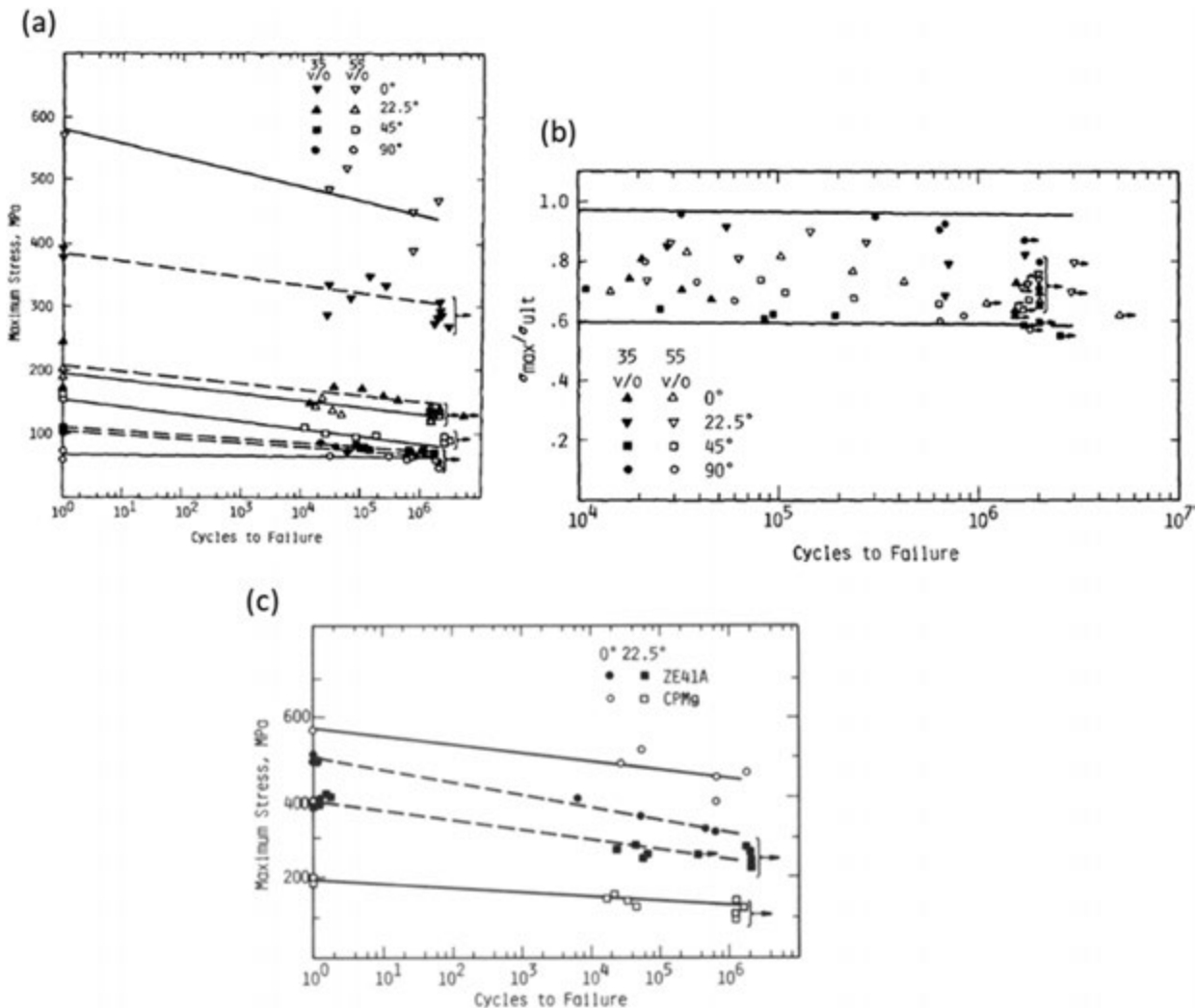


Fig. 15 (a) SN curves for Mg-35% and 55% Al_2O_3 fibers; (b) Normalized fatigue data of Mg-35, 55 Al_2O_3 ; and (c) fiber orientation effects of magnesium reinforced with Al_2O_3 fibers. Reproduced from (b) Reproduced from Hack, J.E., Page, R.A., Leverant, G.R., 1984. Tensile and fatigue behavior of aluminum oxide fiber reinforced magnesium composites: Part I. Fiber fraction and orientation. *Metallurgical Transactions A* 15 (7), 1389. Page, R.A., Hack, J.E., Sherman, R., Leverant, G.R., 1984. Tensile and fatigue behavior of aluminum oxide fiber reinforced magnesium composites: Part II. Alloying effects. *Metallurgical Transactions A* 15 (7), 1397–1405.

Corrosion Fatigue (CF) of Magnesium Matrix Composites

Corrosion fatigue (CF) is another common phenomenon of failure occurring due to the concurrent activity of repeated mechanical loading and aggressive environments i.e. it is the interaction of localized corrosive activity with irreversible cyclic deformation (Birbilis and Hinton, 2011). Typically, it occurs in implant devices when subject to physiological environments; the body fluid has a pH level ranging from 1 to 9 depending on the tissues. (Harandi and Singh Raman, 2017). Magnesium based materials are increasingly being recommended as candidates for temporary implant devices vis-a-vis screws, stents, pins, and bone plates due to their ability to degrade in physiological environment without causing any detrimental or toxic effects and aid in the bone healing process. This biodegradability of magnesium also assists in elimination of secondary surgery for removal of the implant materials. Recently, magnesium matrix composites are increasingly being recommended for biomedical applications due to their low modulus of ~ 45 GPa, very close to the human cortical bone (2–30 GPa) and high specific strengths (Dutta *et al.*, 2020), demonstrating a promising mechanical compatibility with the bone, thereby eliminating stress shielding effects, a common phenomenon for traditional implants such as Co-Cr, Ti64 and stainless steel. While there is no reported literature to the authors' best knowledge on CF of Mg matrix composites, there is some information available on magnesium alloys which could serve as guiding beacon for future research on magnesium matrix composites. Magnesium-Aluminum-Zinc alloys such as AZ91 have shown a rather controlled degradation and increased bone mass around them as demonstrated by Witte *et al.* in guinea pig femora (Witte *et al.*, 2005) and rabbit model (Witte *et al.*, 2007) and no adverse toxicity because of Al present in the matrix. Jafari *et al.*

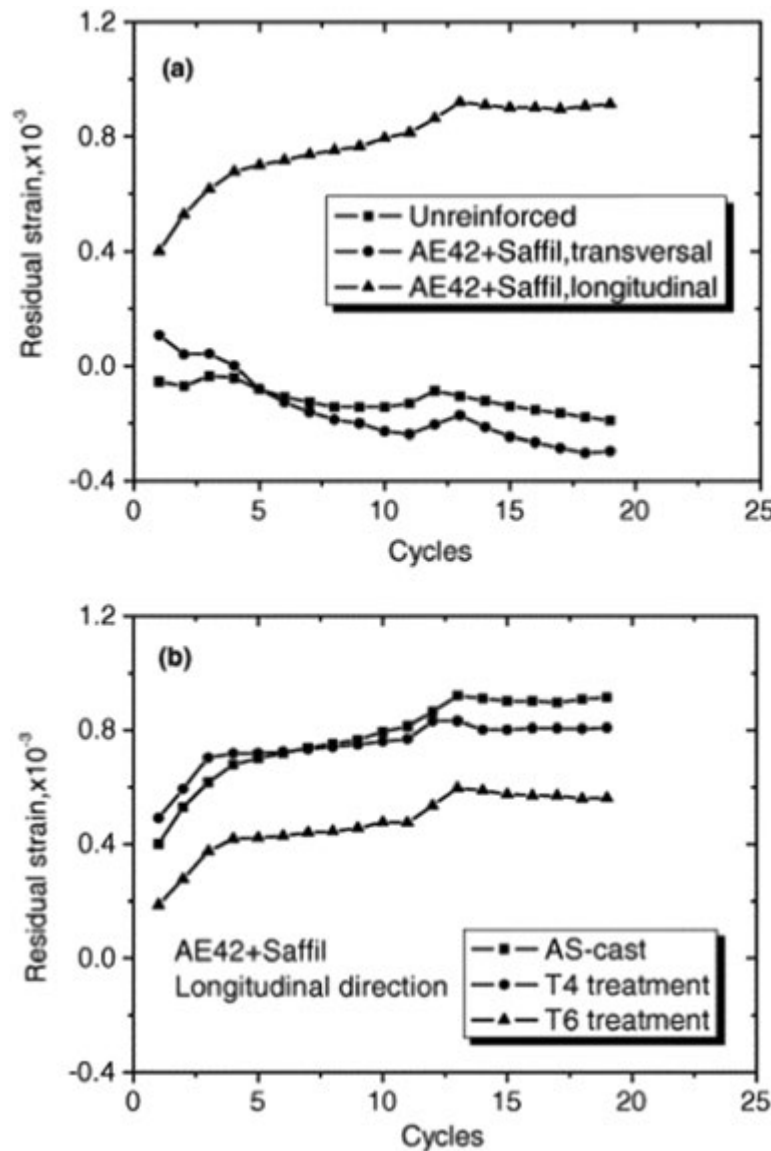


Fig. 16 Residual strain vs thermal cycles of AE42 alloy and its composite (a) in cast condition; and (b) after T4 and T6 treatments. Image reproduced from Huang, Y.D., Hort, N., Dieringa, H., Maier, P., Kainer, K.U., 2006. Investigations on thermal fatigue of aluminum- and magnesium-alloy based composites. *International Journal of Fatigue* 28 (10), 1399–1405.

(2015) investigated CF life of AZ91 alloy and found that the AZ91 alloy was susceptible to CF. While AZ91 alloy undergoes fatigue due to the cracks initiating at inclusions, its fatigue life is much higher in air than in physiological environments such as m-SBF where cracking is enhanced because of pitting and hydrogen embrittlement as shown in Fig. 17(a). Similar studies were also conducted on WE43 alloy which showed a CF limit of 110 MPa in air in contrast to a CF limit of only 40 MPa in SBF as given in Fig. 17(b) (Gu *et al.*, 2010).

While magnesium micro-composites may not demonstrate promise in resistance to CF, with recent advances in magnesium nanocomposites in enhancing mechanical fatigue behavior as discussed above, magnesium nanocomposites would be excellent candidates for temporary implant applications as they not only enhance the corrosion resistance of magnesium, but also its fatigue limit (Johanes *et al.*, 2019). Further, nanoparticles in the magnesium nanocomposites can also be engineered for targeted drug delivery which further enhances the functionality of these potential temporary implant materials. However, there is a dearth in understanding of CF of magnesium nanocomposites in the scientific community and it is imperative to understand the cracking/failure mechanisms of magnesium nanocomposites under physiological environments and cyclic loading conditions to prove the nanocomposites useful for biomedical applications and this would be an exciting direction of research for researchers working in this field and industries commercializing magnesium composites as potential biomaterials.

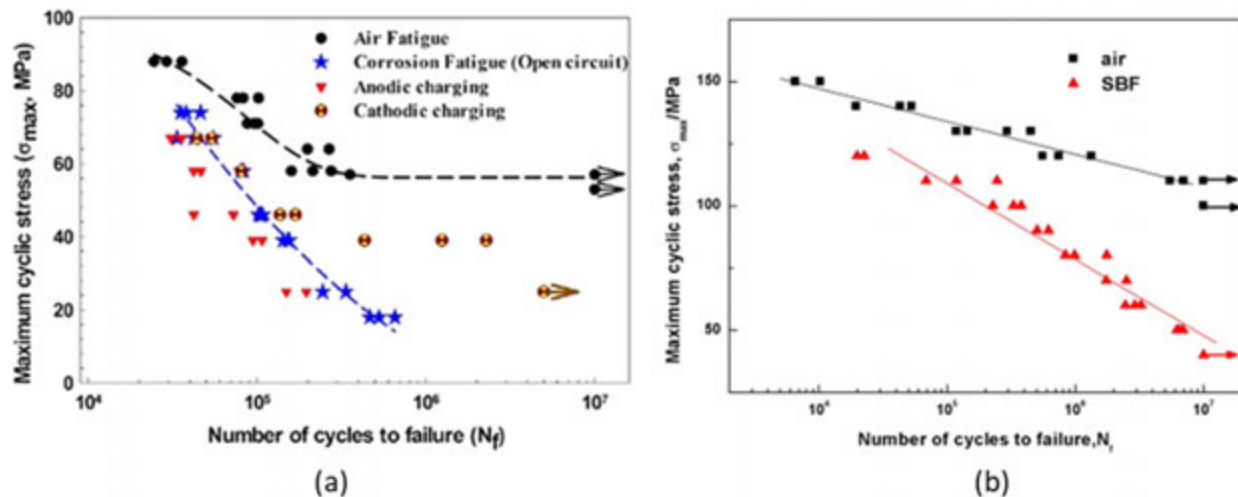


Fig. 17 S-N curve of (a) AZ91D alloy, and (b) WE43 alloy in different environments. Images reproduced from Jafari, S., Singh Raman, R.K., Davies, C.H.J., 2015. Corrosion fatigue of a magnesium alloy in modified simulated body fluid. *Engineering Fracture Mechanics* 137, 2–11. Gu, X.N., Zhou, W.R., Zheng, Y.F., *et al.*, 2010. Corrosion fatigue behaviors of two biomedical Mg alloys – AZ91D and WE43 – In simulated body fluid. *Acta Biomaterialia* 6 (12), 4605–4613.

Summary

Magnesium is an extraordinary candidate for lightweight applications such as in the aerospace, automobile, biomedical and electronic sectors. Because most of the engineering and biomedical applications involve cyclic loading, fatigue life estimation of Mg materials, particularly, composites is extremely critical for the efficient design and implementation of these materials. Under cyclic loads, the crack initiation in Mg materials is related to basal slip and the crack growth follows an intergranular or transgranular mechanism. In general, the crack propagation is faster in the case of Mg composites which can be strongly attributed to the microstructural constituents such as reinforcements. This article presents different aspects of fatigue of magnesium matrix composites, including the role of micron, sub-micron, and nano reinforcements on the fatigue life, followed by the microstructural aspects of the composites. Overall, a significant amount of works on the stress-life (s-N) highlight the role of reinforcements on the fatigue behavior of Mg. For example, the micro reinforcements such as fibers oriented 0° to the loading axis retard the fatigue crack growth while the those oriented 45° to the loading axis accelerate the crack propagation. Tremendous improvements in fatigue strength were also common in the case of nanocomposites that exhibit better interfacial integrity with Mg matrix. Overall, it is essential to note that the reinforcement addition must be incorporated using efficient processing methods that can produce a sound, defect-free microstructure without agglomeration of particles to achieve the best fatigue performance.

References

- Albinmousa, J., 2020. Fatigue of magnesium-based materials. In: Gupta, M. (Ed.), *Magnesium – The Wonder Element for Engineering/Biomedical Applications*. IntechOpen.
- Bayani, H., Saebnoori, E., 2009. Effect of rare earth elements addition on thermal fatigue behaviors of AZ91 magnesium alloy. *Journal of Rare Earths* 27 (2), 255–258.
- Birbilis, N., Hinton, B., 2011. Chapter 19 – Corrosion and corrosion protection of aluminium. In: Lumley, R. (Ed.), *Fundamentals of Aluminium Metallurgy*. Woodhead Publishing, pp. 574–604.
- (ASTM), 2013. ASTM E1823-13:2013: Standard Terminology Relating to Fatigue and Fracture Testing. West Conshohocken, PA: ASTM International.
- Davidson, D.L., Chan, K.S., McMinin, A., Leverant, G.R., 1989. Micromechanics and fatigue crack growth in an alumina-fiber-reinforced magnesium alloy composite. *Metallurgical Transactions A* 20 (11), 2369–2378.
- van der Walde, K., Brockenbrough, J.R., Craig, B.A., Hillberry, B.M., 2005. Multiple fatigue crack growth in pre-corroded 2024-T3 aluminum. *International Journal of Fatigue* 27 (10), 1509–1518.
- Dutta, S., Gupta, S., Roy, M., 2020. Recent developments in magnesium metal–matrix composites for biomedical applications: A review. *ACS Biomaterials Science & Engineering* 6 (9), 4748–4773.
- Gu, X.N., Zhou, W.R., Zheng, Y.F., *et al.*, 2010. Corrosion fatigue behaviors of two biomedical Mg alloys – AZ91D and WE43 – In simulated body fluid. *Acta Biomaterialia* 6 (12), 4605–4613.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46.
- Harandi, S.E., Singh Raman, R.K., 2017. Corrosion fatigue of a magnesium alloy under appropriate human physiological conditions for bio-implant applications. *Engineering Fracture Mechanics* 186, 134–142.
- Huang, Y.D., Hort, N., Dieringa, H., Maier, P., Kainer, K.U., 2006. Investigations on thermal fatigue of aluminum- and magnesium-alloy based composites. *International Journal of Fatigue* 28 (10), 1399–1405.
- Inoue, A., 1995. High strength bulk amorphous alloys with low critical cooling rates (overview). *Materials Transactions, JIM* 36 (7), 866–875.
- Jabbari, A.H., Delavar, H., Sedighi, M., 2020. High cycle fatigue behavior of magnesium matrix nanocomposite at elevated temperatures. *Mechanics of Materials* 142, 103278.
- Jafari, S., Singh Raman, R.K., Davies, C.H.J., 2015. Corrosion fatigue of a magnesium alloy in modified simulated body fluid. *Engineering Fracture Mechanics* 137, 2–11.

- Johanes, M., Tekumalla, S., Gupta, M., 2019. Fe₃O₄ nanoparticle-reinforced magnesium nanocomposites processed via disintegrated melt deposition and turning-induced deformation techniques. *Metals* 9 (11), 1225.
- Llorca, J., 1994. The cyclic stress-strain curve of discontinuously-reinforced Al-and Mg-based composites. *Scripta Metallurgica et Materialia* 30 (6), 755–760.
- Mayencourt, C., Schaller, R., 2002. Mechanical-stress relaxation in magnesium-based composites. *Materials Science and Engineering: A* 325 (1), 286–291.
- Min, Y., Akbulut, M., Kristiansen, K., Golan, Y., Israelachvili, J., 2008. The role of interparticle and external forces in nanoparticle assembly. *Nature Materials* 7, 527–538.
- Nafar Dastgerdi, J., Marquis, G., Sankaranarayanan, S., Gupta, M., 2016. Fatigue crack growth behavior of amorphous particulate reinforced composites. *Composite Structures* 153, 782–790.
- Nunes, J., Chin, E.S., Slepetz, J.M., Tsangarakis, N., 1986. Tensile and fatigue behavior of alumina fiber reinforced magnesium composites. *Metallurgical Transactions A* 15, 1397–1405.
- Page, R.A., Hack, J.E., Sherman, R., Leverant, G.R., 1984. Tensile and fatigue behavior of aluminum oxide fiber reinforced magnesium composites: Part II. Alloying effects. *Metallurgical Transactions A* 15 (7), 1397–1405.
- Qi, L., Ju, L., Zhou, J., *et al.*, 2017. Tensile and fatigue behavior of carbon fiber reinforced magnesium composite fabricated by liquid-solid extrusion following vacuum pressure infiltration. *Journal of Alloys and Compounds* 721, 55–63.
- Ramalingam, V.V., Ramasamy, P., Kovukkal, M.D., Myilsamy, G., 2020. Research and development in magnesium alloys for industrial and biomedical applications: A review. *Metals and Materials International* 26 (4), 409–430.
- Sabet, A., Jabbari, A., Sedighi, M., 2018. Microstructural properties and mechanical behavior of magnesium/hydroxyapatite biocomposite under static and high cycle fatigue loading. *Journal of Composite Materials* 52 (13), 1711–1722.
- Srivatsan, T.S., Al-Hajri, M., Lam, P.C., 2005. The quasi-static, cyclic fatigue and final fracture behavior of a magnesium alloy metal-matrix composite. *Composites Part B: Engineering* 36 (3), 209–222.
- Srivatsan, T.S., Godbole, C., Paramsothy, M., Gupta, M., 2012a. Influence of nano-sized carbon nanotube reinforcements on tensile deformation, cyclic fatigue, and final fracture behavior of a magnesium alloy. *Journal of Materials Science* 47 (8), 3621–3638.
- Srivatsan, T.S., Manigandan, K., Godbole, C., Paramsothy, M., Gupta, M., 2012b. Influence of nickel particle reinforcement on cyclic fatigue and final fracture behavior of a magnesium alloy composite. *Metals* 2 (2), 143–169.
- Srivatsan, T.S., Godbole, C., Quick, T., Paramsothy, M., Gupta, M., 2013. Mechanical behavior of a magnesium alloy nanocomposite under conditions of static tension and dynamic fatigue. *Journal of Materials Engineering and Performance* 22 (2), 439–453.
- Tekumalla, S., Bibhanshu, N., Shabadi, R., *et al.*, 2018. Evolution of texture and asymmetry and its impact on the fatigue behaviour of an in-situ magnesium nanocomposite. *Materials Science and Engineering: A* 727, 61–69.
- Tekumalla, S., Bibhanshu, N., Suwas, S., Gupta, M., 2019. Superior ductility in magnesium alloy-based nanocomposites: The crucial role of texture induced by nanoparticles. *Journal of Materials Science* 54 (11), 8711–8718.
- Tekumalla, S., Shabadi, R., Yang, C., Seetharaman, S., Gupta, M., 2017. Strengthening due to the in-situ evolution of δ 1' Mg-Zn rich phase in a ZnO nanoparticles introduced Mg-Y alloy. *Scripta Materialia* 133, 29–32.
- Tevatia, A., Srivastava, S.K., 2015. Modified shear lag theory based fatigue crack growth life prediction model for short-fiber reinforced metal matrix composites. *International Journal of Fatigue* 70, 123–129.
- Witte, F., Kaese, V., Haferkamp, H., *et al.*, 2005. In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials* 26 (17), 3557–3563.
- Witte, F., Ulrich, H., Palm, C., Willbold, E., 2007. Biodegradable magnesium scaffolds: Part II: Peri-implant bone remodeling. *Journal of Biomedical Materials Research Part A* 81A (3), 757–765.

High-Temperature Properties of Metal Matrix Composites

Oluseyi P Oladijo, Botswana International University of Science and Technology, Palapye, Botswana and University of Johannesburg, Johannesburg, Gauteng, South Africa

Samuel A Awe, Automotive Components Floby AB, Floby, Sweden

Esther T Akinlabi, Pan African University for Life and Earth Sciences Institute, Ibadan, Nigeria

Resego R Phiri, Lebudi L Collious, and Rebaone E Phuti, Botswana International University of Science and Technology, Palapye, Botswana

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal is one of the significant engineering materials known to man, which has been and is still being used in various technological applications. Interestingly, due to the advancement in scientific knowledge and technical know-how, there is a desire for new materials that could fulfill the specific requirements for different engineering applications, which could not be solely obtained from the metallic material. This led to the combination of metal/metal alloy with ceramic materials forming what is called metal matrix composites.

Metal matrix composites (MMCs) are advanced engineering materials consisting of metal (e.g., Al, Cu, Mg, Ti) as the matrix and the second reinforcing/strengthening phase (e.g., Al_2O_3 , Cr_2O_3 , SiC, TiC, B_4C , Cr_3C_2 , BN, Si_3N_4 , carbon nanotubes, etc.) to produce properties different from the parent or constituent materials. The reinforcing phase enhances the needed strength and stiffness properties of the composites, and this strengthening phase could be in the form of short/discontinuous fibers/whiskers or continuous fibers or particulates. **Fig. 1** illustrates the different categories of metal matrix composites based on the geometric forms (shape and dimensions) of the strengthening phase.

In general, the reinforcement of composite materials serves different purposes based on the specific needs for their desired applications. In many instances, all the expected material properties for a particular application may not be found in a single monolithic material; hence, the need to combine two or more materials to achieve these desired properties. Some of these properties ([Kainer, 2006](#); [Chung, 2010](#); [Macke et al., 2012](#)) for which composites are made are highlighted below:

- Improved yield and tensile strengths at ambient and elevated temperatures.
- Increased stiffness at room and high temperatures.
- Enhanced chemical and corrosion resistance.
- Increased thermal insulation or conductivity.
- Improved thermal shock stability.
- Increased electrical insulation or conductivity.
- Improved fatigue resistance, especially at higher temperatures.
- Enhanced abrasion and wear resistance.

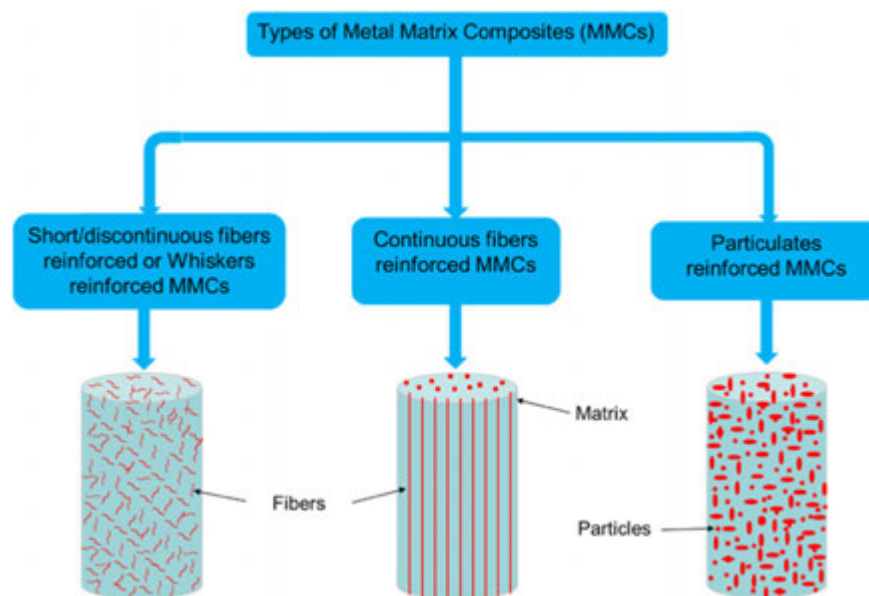


Fig. 1 Categories of metal matrix composites based on the reinforcement forms.

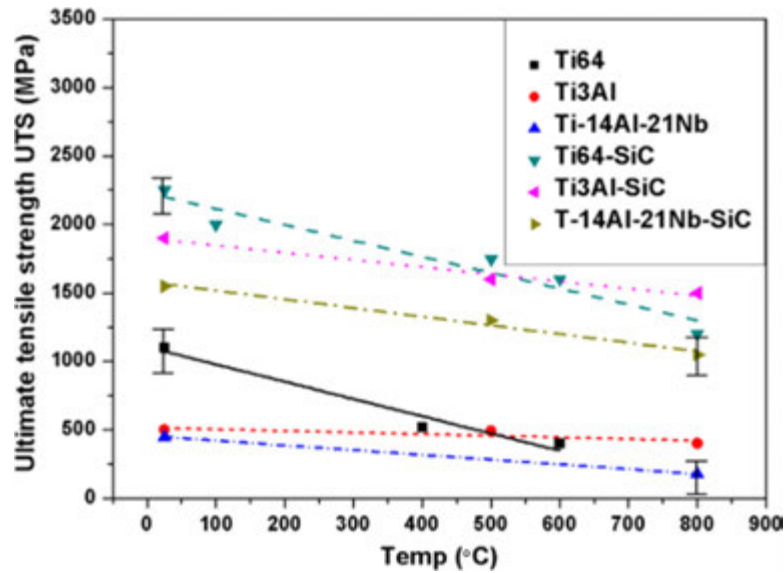


Fig. 2 Effect of temperature on the strength of titanium alloys and titanium matrix composites. Reproduced from Hayat, M.D., *et al.*, 2019. Titanium metal matrix composites: An overview. Composites Part A: Applied Science and Manufacturing 121, pp. 418–438. doi:[10.1016/j.compositesa.2019.04.005](https://doi.org/10.1016/j.compositesa.2019.04.005).

- Controlled thermal expansion coefficient.
- Reduced material weight (low density).
- Improved fracture toughness and damage tolerance.
- Improved creep resistance.
- Enhanced energy absorption and vibration damping capabilities.
- Improved electromagnetic shielding effectiveness.

Interestingly, due to the possibility that the properties of composite materials can be engineered to fit the desired engineering application, composites have been employed in the design and manufacturing of diverse engineering components in various technological sectors. For example, composite materials have been used in marine, automotive, aerospace, energy, biomedical, electronics, cutting tools, construction, and defense industries. However, in this section, more attention shall be focused on the high-temperature properties of MMC materials and their subsequent applications in engineering design and components manufacturing.

High-Temperature Properties of MMCs

High-temperature properties of engineering materials are a vital concern in many applications such as power generation, aerospace, and automotive. This is because temperature plays a crucial role in determining the functionality and applicability of materials in specific technological applications. Fig. 2 depicts the influence of temperature on the ultimate tensile strength of titanium alloys and their composites. It is noticeable that the strength of these materials decreases with increasing temperature. However, it is noteworthy that the addition of SiC reinforcing particles to the titanium alloys enhances their temperature retention capacity. This behavior indicates that MMC materials have high thermal stability compared to their respective matrix alloys. For instance, some aluminum alloys cannot be used for a component serving at temperatures above 200°C since an increase in temperature beyond this affects their microstructure and mechanical properties significantly. Exposure to elevated temperature decreases the mechanical integrity as well as the oxidation resistance of most metallic alloys. Through a proper combination of the right ceramic reinforcement with the suitable matrix, the high-temperature properties of the resulting MMC can be improved.

High-Temperature Applications of MMCs

The choice of using metal-matrix composites for several high-temperature applications is dictated by their attributes, which can be tailored to suit the desired component design. Some of these attributes include high specific strength, high specific modulus, high-temperature strength retention, excellent creep, fatigue, and wear resistance. Due to the possibility to withstand high temperatures, MMC materials are used in resistors and other electronic components.

In the automotive industry, elevated-temperature applications are primarily concerned with the engines, transmission, and braking components (Nturanabo *et al.*, 2013). These components could experience temperatures higher than 300°C during service, which could substantially reduce the mechanical reliability of the components. For example, the automotive brake disks are

usually exposed to extreme temperatures as high as 700°C during braking. This severe temperature may lead to buckling, thermoelastic instability, thermal cracks, premature wear, brake fade, brake squeal and judder, bearing failure, phase transformation (especially in cast iron), or fatigue cracks on a disc surface (Thomas *et al.*, 2019). Aluminum and magnesium alloys have been prominent in automobile applications in recent times due to their lightweight characteristic. Unfortunately, it is somehow challenging to apply most of these lightweight alloys (e.g., Al and Mg alloys) directly for components, such as engine blocks, powertrains, and braking systems, serving in the severe working environment due to their relatively low strength and modulus, and poor wear properties at elevated temperatures (Shin *et al.*, 2019). By reinforcing these low-density alloys with ceramic materials, their specific strength, high-temperature strength, thermal stability, as well as their creep, fatigue, and wear resistance, can be improved, therefore, qualifying them as potential materials for replacing cast iron and other materials in engine and brake applications. Below are the major components that have been produced from MMC materials, especially aluminum matrix composite, for automobile applications.

The automobile brake disc or drum is a crucial component of the brake system, which is attached to the wheels of a car. When brakes are applied to a moving vehicle, a significant amount of power is generated in the form of kinetic energy. This kinetic energy is subsequently converted into thermal energy through the friction losses between the brake disc/drum and the pads. The brake disks are subsequently subjected to a high level of thermal load, which results in a sudden increase in the temperature of the system as high as 700°C (Thomas *et al.*, 2019). These brake components are predominantly manufactured from gray cast iron due to its good castability and machinability, high thermal conductivity and specific heat capacity, high scuffing resistance, high melting point, and high friction factor and strength, and lower cost (Rashid, 2014). The major disadvantage of the conventional brake disc material is its weight, which significantly impacts on the vehicle's fuel consumption and its low wear resistance that generates non-exhaust particle emissions, which are of most significant concern in recent times. This challenge has led many automakers to seek for alternative brake disc materials. Silicon carbide particles reinforced aluminum alloys (Al-MMCs) have attracted more attention for this purpose due to their tailorable attributes, including high specific strength and stiffness, excellent wear and friction performance, high thermal conductivity and creep resistance, high energy absorption and damping capacity, good oxidation, and corrosion resistance, and low thermal expansion (Stojanović and Ivanović, 2015; Thomas *et al.*, 2019). Fig. 3 shows a typical automobile MMC brake disc and drum that had been installed on different car models. For instance, MMC brake disks had been used in various vehicle models, including the Lotus Elise, Chrysler Prowler, General Motors EV1, Volkswagen Lupo 3L, Volvo V40 and the Toyota RAV4-EV (Macke *et al.*, 2012).

However, the primary concern for not fully adopting Al-MMC brake disks by the various automakers is their temperature withstanding capacity, which has been recognized as a design issue (Allison and Cole, 1993). Good thermal conductivity and high specific heat are the desirable properties of Al-MMC materials that make them suitable alternative automotive brake disc materials.



Fig. 3 A typical MMC brake drum (a) and disc (b), and installed MMC brake disc.

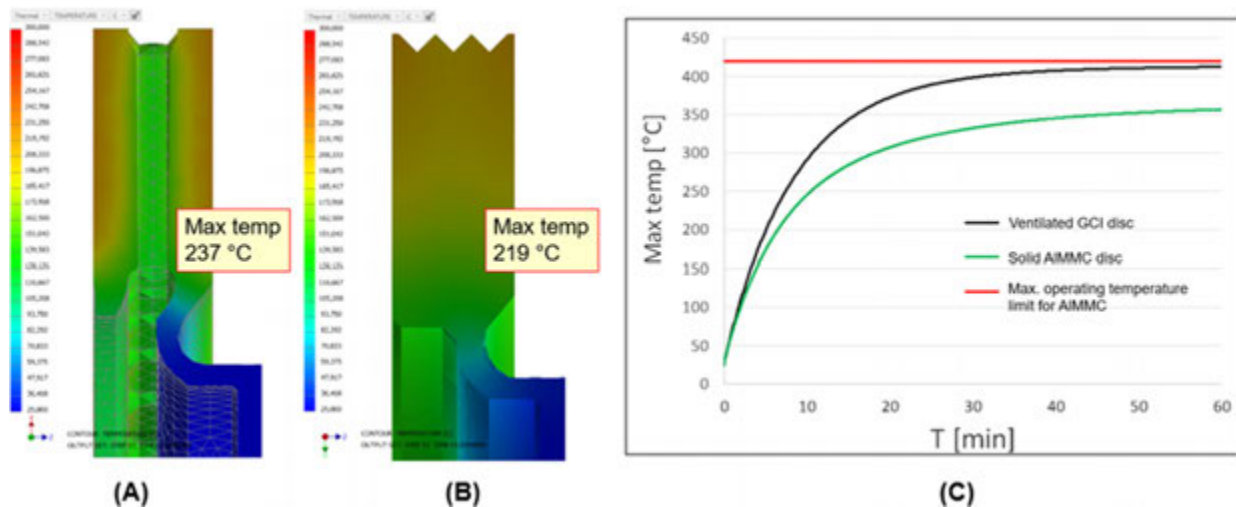


Fig. 4 Temperature distribution in (A) ventilated gray cast-iron (GCI) and (B) solid Al-MMC brake disks during a single stop from 190 to 0 km/h, and (C) during Alpine descent at a constant speed of 20 km/h over 20 min period. Reproduced from Thomas, A., Zervos, N., Eklund, A., Awe, S.A., 2019. Simulation study on the thermomechanical behavior of Al-MMC automotive brake disks. In: Eurobrake 2019. Dresden: FISITA, pp. 1–12.

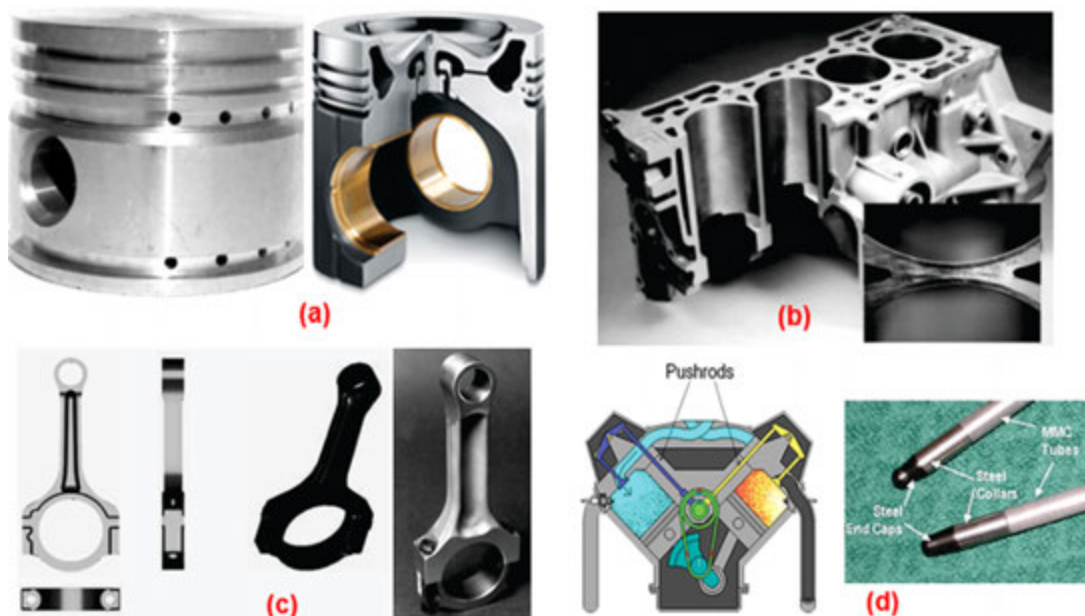


Fig. 5 Typical pistons (a), engine block with cylinder barrel (b), connecting rods (c), and pushrods (d) made of Al-MMCs. Reproduced from Stojanović, B., Ivanović, L., 2015. Primjena aluminijevskih hibridnih kompozita u automobilske industriji. Tehnicki Vjesnik 22 (1), pp. 247–251. doi:10.17559/TV-20130905094303.

This implies that by carefully harnessing the Al-MMC properties when designing brake disc, the heat generated during braking can both be absorbed and dissipated more quickly, and consequently prevent temperature accumulation. The results of the recent simulation study reveal that the Al-MMC disc can perform comparably to the standard brake disks (Thomas *et al.*, 2019). Fig. 4(A) and (B) showed the temperature distribution in both the regular and Al-MMC brake disks when they were subjected to an abrupt stop from 190 km/h. The maximum temperature in the Al-MMC disc is approximately 8% lower than that of the conventional disc. The simulation results also depict that the maximum temperatures experienced by both GCI and Al-MMC disks after a downhill drive (Alpine descents) at a constant speed of 20 km/h for 60 min are 315 and 260 °C, respectively. This indicates that Al-MMC disc experienced about 17% lower temperature than the GCI disc, which is attributed to the excellent thermal conductivity and adequate geometry design of the Al-MMC disc.

Besides the brake disks, the other automotive components that have been produced from Al-MMCs are the pistons, connecting rods, engine cylinders, and pushrods, as shown in Fig. 5. These components serve under harsh conditions where the thermal

conductivity, thermal stability, low weight, and thermal expansion, excellent resistance to oxidation and wear, and high-temperature strength retention of Al-MMCs become beneficial. Engine pistons made of Al-MMC have been manufactured and used in Toyota diesel engine cars, and they are also commonly used in Asia and West Europe car producers. Also, the engines with cylinder barrel produced from Al-MMC material had been installed on Honda S2000 – sports cars, Acura NSX cars type, Porsche Bower motors, and Toyota Celica 2000 cars (Stojanović and Ivanović, 2015).

In the aerospace industry, MMC materials are used because of their high stiffness (Young's modulus), high specific strength, low coefficient of thermal expansion, enhanced strength retention at high temperature coupled with high thermal conductivity. The materials suitable for aerospace applications should be lightweight and possess the capacity to withstand elevated temperatures for a prolonged time in aggressive environments. However, by incorporating a suitable high-temperature ceramic fibers into an appropriate metal matrix, potential lightweight MMCs with the right high-temperature properties can be made. However, further research investigations are still required in this regard.

Most materials, especially the superalloys that are used in aircraft and power generation turbine components, are usually subjected to an extremely oxidizing working environment and elevated temperatures for reasonable periods. As a result of these severe serving conditions, the mechanical integrity of these materials is sometimes affected. Furthermore, the wear resistance of these superalloys at elevated temperatures is relatively low, leading to an increase in maintenance operations (Verdi *et al.*, 2017). MMC coatings with Ni-based superalloys matrices are developed to avoid such compromise and applied to enhance the mechanical integrity of the components. This MMC coating has considerably improved the maintenance situation of such components.

High-Temperature Mechanical Properties

The stress-strain curve provides the basic mechanical properties of MMCs. These properties include stiffness (young's modulus), yield strength, ultimate tensile strength and ductility. During high temperature operation of MMCs, dislocations strongly influence these strength properties and others like fatigue resistance and creep resistance thus affecting the performance of these composites. Generally, the young's modulus, yield strength and ultimate tensile strength of MMCs decrease with increasing temperature. Young's modulus and ultimate tensile strength of $\text{Al}_2\text{O}_3/\text{A6061}$ MMCs measured at room temperature, 170 and 220°C was observed to decrease with increasing temperature (Tanaka *et al.*, 1996). This was also observed by Garcia-Leiva *et al.* (2003) with $\text{Ti64}/\text{SiC}$ MMCs with tests performed at room temperature, 55 and 600°C. Lakshmikantha and Auradi (2020) studied $\text{Al}/\text{B}_4\text{C}$ particulate MMCs at 100 and 200°C, the ultimate tensile strength of the composites decreased with increasing temperature. Oñoro *et al.* (2009) reinforced A6061 and A7015 aluminum alloys with B_4C particles and tested their ultimate tensile strength at room temperature and elevated temperatures ranging from 200 to 500°C. The ultimate tensile strength was also observed to decrease gradually up to 200°C before an abrupt decrease. Liu *et al.* (2019) investigated the ultimate tensile strength of CNT's/Cu MMCs in the temperature range of 25–655°C and similar observations were made as with the other authors.

The decrease in young's modulus and ultimate tensile strength of MMCs with increasing temperature is mainly attributed to the softening of the metal matrix at elevated temperatures. Generally, the decrease is gradual in the temperature range of 25–200°C. As the temperature increases in this range, the mobility of dislocations increases causing them to slip thereby reducing the work hardenability of the MMCs. Once temperatures go beyond 200°C, dynamic recovery occurs in which dislocations begin to move, annihilate and rearrange into more stable configurations with relaxed interactions with neighboring dislocations thus causing a decrease in the strength of MMCs. Due to the increased plasticity due to dislocation motion at high temperatures, the ductility of MMCs generally increases with increasing temperature as shown by Oñoro *et al.* (2009). Other several factors that may result in a reduction in young's modulus, yield strength and ultimate tensile strength of MMCs with increasing temperature include the brittle fracturing of the reinforcing material and/or debonding at the interface between the matrix and the reinforcement. This may be caused by a mismatch in the thermal expansion coefficients of the matrix metal and the reinforcement. As the temperature increases, the expansion of the matrix metal is restricted by the reinforcement thus leading to the generation of thermal residual stresses at the matrix/reinforcement interface consequently affecting load transfer from the matrix to the reinforcement during high temperature operation. These residual stresses deteriorate the matrix/reinforcement interface and are often relieved through elastic relaxation and plastic deformation.

Materials subjected to static and elastic loads for a long period of time plastically deform in a process known as creep. At room temperature creep is negligible for most materials and only becomes significant at high service temperatures. Creep occurs in metals when they are required to operate at temperatures above 30%–40% of their absolute melting point. Creep curves (plots of increasing strain against time) provide an important property called the steady-state creep rate used to describe the creep behavior of materials subjected to certain loads at given temperatures. Generally, creep curves of materials can be divided into three distinct regions namely primary creep in which the creep rate decreases with increasing time due to strain hardening, secondary creep where the creep rate is nearly constant (steady-state creep rate) due to competing contributions from strain hardening and plastic deformation and lastly tertiary creep in which materials begin to neck and cavitate thus increasing the creep rate.

The dependence of the creep rate on the applied stress and temperature for metals and alloys can be described by the Norton equation given by;

$$\dot{\epsilon}_s = \frac{ADGb}{kT} \cdot \left(\frac{\sigma}{G}\right)^n \quad (1)$$

where A and n (the stress exponent) are material dependent creep constants, G is the shear modulus, b the Burgers vector, k the Boltzmann constant, T is the absolute temperature and σ the applied stress (Viswanath, *et al.*, 2015). The diffusion coefficient D is given by

$$D = D_0 \cdot e^{\left(\frac{-Q_C}{RT}\right)} \quad (2)$$

where D_0 is the frequency factor and Q_C the creep activation energy (Viswanath *et al.*, 2015). The stress exponent, n may take values ranging from 3, 5, 7 and 8 which provides information on the mechanism controlling the creep rate. A value of $n = 3$ indicates creep governed by the viscous glide of dislocations (Mohamed and Langdon, 1974), $n = 5$ and $n = 7$ represents creep controlled by dislocation climb at high and low temperatures, respectively (Sherby and Burke, 1968; Robinson and Sherby, 1969), and $n = 8$ shows creep controlled by lattice diffusion (Sherby, *et al.*, 1977). However, it should be noted that MMCs show no secondary creep region (steady-state creep) but rather a sudden transition from primary to tertiary creep resulting in a minimum creep rate. Therefore using Eq. (1) to calculate the creep rate of MMCs results in much higher values of the stress exponent than those observed with creep of pure metals and simple alloys (Evans and Knowles, 1980; Clauer and Hansen, 1984). The stress term in Eq. (1) is however often modified to an effective value to give stress exponents in the range of those of metals and alloys (Viswanath *et al.*, 2015).

The high temperature creep behavior of stir cast AZ91-SiCp composites investigated at 175°C under different stresses revealed a stress exponent ranging from 5.4 to 5.8 indicating that creep in composites was mainly attributed to high temperature dislocation climbing (Viswanath *et al.*, 2015). The same creep mechanism was also reported in SiCw/Al-Fe-V-Si composites tested at temperatures ranging from 300 to 450°C (Peng and Zhu, 2003).

In MMCs, ceramic reinforcements are characterized by extremely high resistance to creep, therefore the creep rate of MMCs at elevated temperatures is mostly governed by the movement of dislocations in the matrix. Dislocation movement in the matrix during creep occurs through dislocation slip or dislocation climb. The former occurs at all temperatures above absolute zero whilst the latter only occurs at high temperatures. Ceramic reinforcements in MMCs are able to restrict plastic flow in the matrix under elastic loads at room temperature, however, upon raising the temperature to creep conditions, atoms in the matrix gain enough mobility to cause dislocations to climb over the reinforcing fibers thus facilitating plastic deformation and hence increasing the creep rate. Moreover, new slip systems are generated at elevated temperatures further increasing dislocation movement and consequently the creep rate. The creep rate of MMCs can also be increased by the relative sliding of grains in the matrix due to plastic flow at the grain boundaries. This deformation process known as grain boundary sliding increases with temperature thus resulting in increased creep rates.

Fatigue resistance is one of the most crucial property for MMCs with applications in the aerospace and the automotive industry. Fatigue is associated with mechanical failure due to formation and growth of cracks in materials subjected to cyclic loads. Failure through fatigue usually occurs after a number of load cycles and strongly depends on service environments like temperature. The fatigue strength of MMCs generally decrease with increasing temperature. This was confirmed through investigations by Ochi *et al.* (2004) on the fatigue properties of $Al_2O_3/A6061$ MMCs at room temperature and elevated temperatures of 200, 350, 400 and 450°C. Fatigue failure of MMCs is characterized by localized plastic deformation in the matrix usually at creep temperatures. This causes the initiation of cracks at grain boundaries which may coalesce upon repeated loading thus ultimately leading to fracture. Moreover, the matrix/reinforcement interface is often a crack initiation site in MMCs due to the accumulation of thermal residual stresses and increased dislocation density at high temperature operation.

High-Temperature Corrosion Properties

High Temperature Oxidation

When exposed to high service temperatures, materials usually experience a degradation in their properties which is caused by chemical interaction between the material and the surrounding environment. Depending on the nature of the environment in which the material is exposed to, the metal can experience, hot corrosion, oxidation and sulfidation. Oxidation takes place when a metal reacts with atmospheric oxygen at elevated temperature. This chemical reaction results in formation of an oxide layer on the metal which may provide protection against further reaction of the metal and the environment that is only if the oxide layer is non-porous and adherent to the metal.

Oxidation of Pure Metals

When oxidized at high temperatures, a pure metal can form a single or multiple oxides and to show which oxide is formed at a particular temperature and partial pressure of oxygen the Ellingham diagram is used as a guide. The Ellingham diagram uses the thermodynamic principles to predict whether the pure metal can be oxidized or not at a particular temperature or and oxygen partial pressure. Taking Magnesium for instance, at very high temperatures magnesium oxidizes to form a single oxide of MgO as shown on the Ellingham diagram.

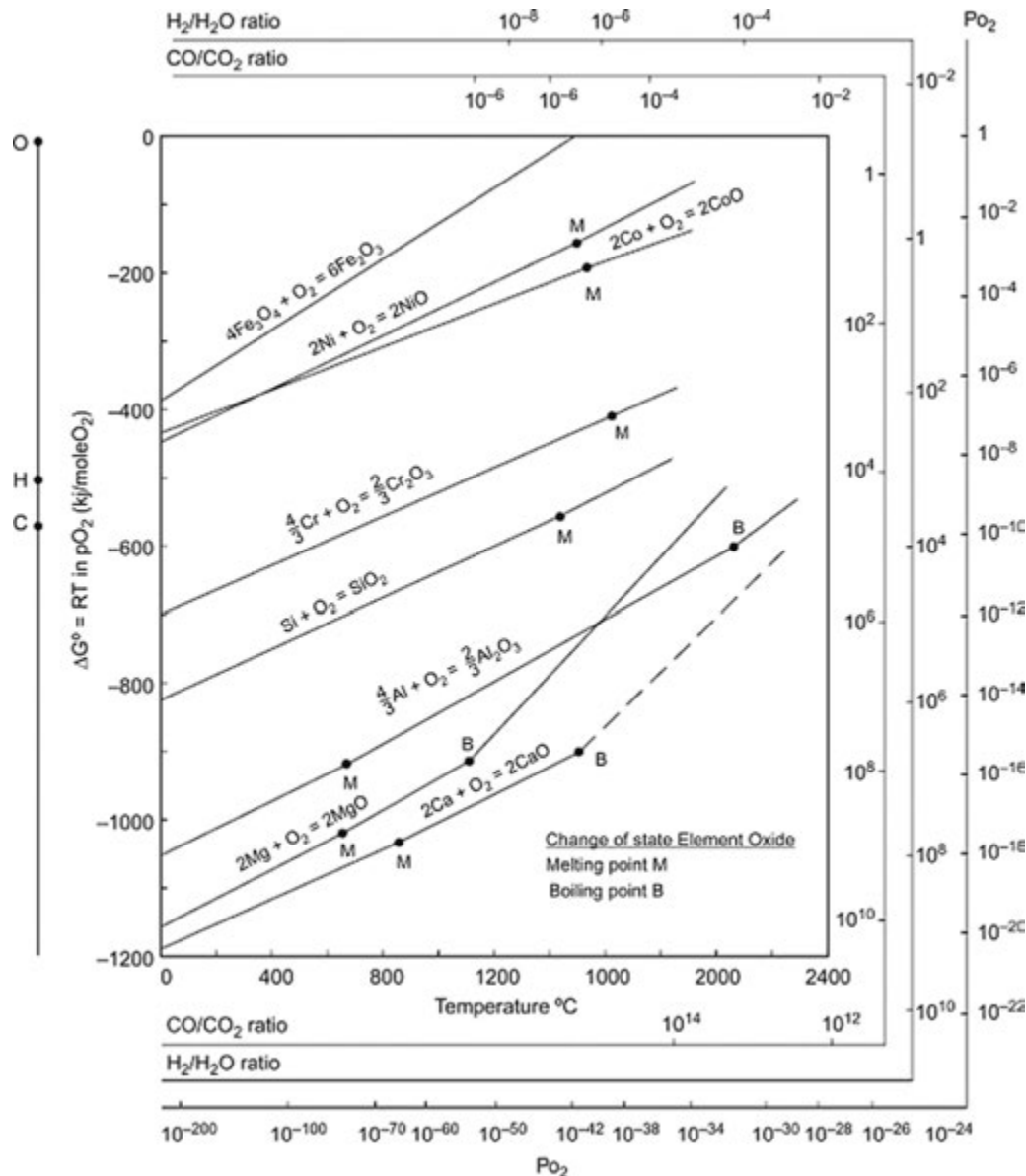


Fig. 6 The Ellingham diagram. Reproduced from Khanna, A.S., 2018. Chapter 6 – High-temperature oxidation. In: Kutz, M. (Ed.), Handbook of Environmental Degradation of Materials, third ed. William Andrew Publishing, pp. 117–132. doi:10.1016/B978-0-323-52472-8.00006-X.

Oxidation of Alloys

Unlike pure metals which have their oxidation relatively simple, oxidation of alloys is a bit complex as several oxides can form as the metallic elements constituting the alloy form their respective oxides based on the temperature and the partial pressure of oxygen. Although several oxides are shown to form as per the Ellingham diagram shown in Fig. 6, only the most stable ones will be retained whereas the less stable one vanishes with time. Also, this is not a straightforward process as there are a number of factors which include the concentration of alloying elements, stability of oxides of the constituting elements and their diffusion constants which determine the oxide layer to be formed.

Oxidation Kinetics

Oxidation kinetics is the variation of the oxidation rate with time. This is an important concept as it allows an engineer to be able to predict the life time of a component serving in high temperatures. The variation of the oxidation rate with time can be, logarithmic, parabolic or linear. From the three variations the parabolic variation shown in Fig. 7 is the most important and it states that the oxide layer formation is inversely proportional related to time, that is as the time increases the rate at which the

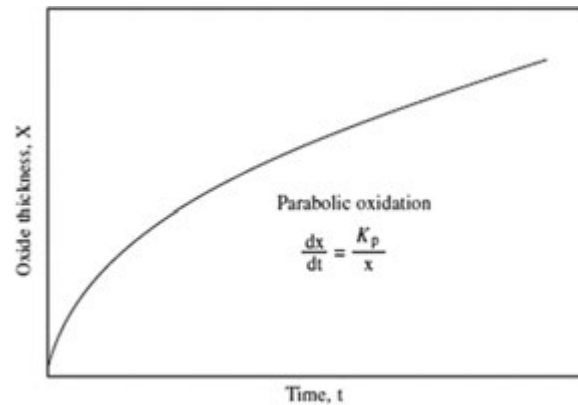


Fig. 7 Parabolic Kinetic behavior. Reproduced from Khanna, A.S., 2018. Chapter 6 – High-temperature oxidation. In: Kutz, M. (Ed.), Handbook of Environmental Degradation of Materials, third ed. William Andrew Publishing, pp. 117–132. doi:[10.1016/B978-0-323-52472-8.00006-X](https://doi.org/10.1016/B978-0-323-52472-8.00006-X).

oxide layer forms decreases continually. The bases of this law is that the oxidation process is governed by diffusion of either the metal ions diffusing from the metal towards the interface of the metal and oxide layer to react with oxygen and as the oxide layer that results from this reaction forms and grows slowly. The reacting metal ions and oxygen atoms take a longer time to diffuse through the oxide layer to the metal/oxygen interface where the reaction happens. This behavior is followed by most high temperature metals and alloys. As a result, components fabricated using such materials tend to have longer service life in high temperature environments.

It is very important to select the right material for fabrication of different industrial components for high temperature applications. The selection requirements for high temperature materials are:

- (1) Microstructural stability.
- (2) High melting point.
- (3) Maintain mechanical properties such as ultimate tensile strength, creep and fatigue strength.
- (4) Low corrosion rate.

Metals used for the fabrication of components for high temperature applications require great microstructural stability at high temperature so as to ensure that the material properties do not change as a result of change in the microstructure. In addition, one important aspect is high melting temperature of the metal, this ensures that the metal can be used for high temperature applications and it is also important that at those high temperatures, the metal should still maintain its tensile strength, fatigue strength and creep (Khanna, 2018).

High Temperature Tribological Properties

There is an increasing demand for high performance materials that can withstand extreme operational conditions experienced in modern industries and operations such as large loadings, high velocity moving contact components and high temperature operations. This has resulted in the emergence of research into high temperature tribological properties and applications of MMCs, due to the limitations presented by metals and alloys. The primary tribological parameters that controls the friction and wear behavior of MMCs include the mechanical and physical factors extrinsic to the material experiencing surface interactions such as sliding velocity, normal loading, surface finish and temperature. The material intrinsic factors such as MMC matrix microstructure, reinforcement type, size and reinforcement shape and amount will also control the tribological performance. Temperature is one of the important key parameter influencing the tribological properties of MMCs. The effect of temperature on the tribological behavior due to changes in sliding speeds and normal loads have demonstrated that the wear performance is directly influenced by the composite thermal properties namely; the thermal conductivity of the matrix as well as the reinforcement (Vissutipitukul and Aizawa, 2005). It has also been noted that the presence of composite defects such as voids and porosity can reduce the mechanical and tribological properties of MMCs (Naplocha and Granat, 2008). Generally, a material is considered to possess good tribological behavior if it has either a low value of coefficient of friction or if it has low wear rate indicating that the degradation rate was low.

Frictional Behavior

It is generally established that almost all real surfaces no matter how carefully prepared are rarely smooth. They are gently undulating and consist of macroscopic and microscopic asperities. The friction between such surfaces in contact emanates from the interaction at these points of asperities where actual or true contact takes place. During these interactions, there will be adhesion of

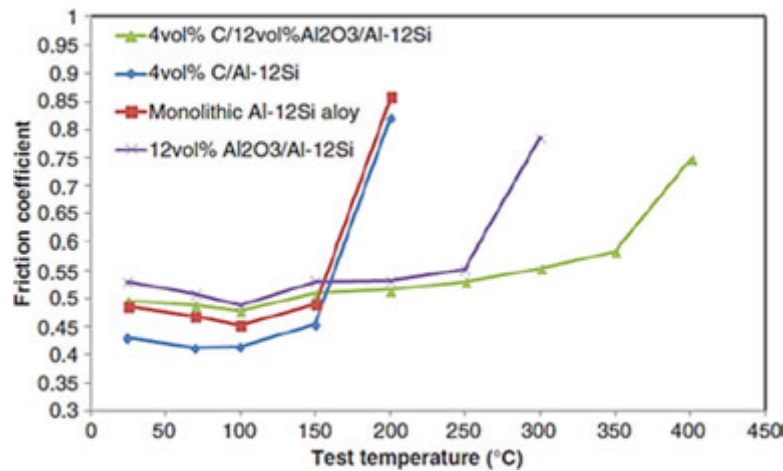


Fig. 8 Variations of coefficient of friction with temperature for Al based alloys. Reproduced from Menezes, P.L., Ingole, S.P., Nosonovsky, M., Kailas, S.V., Lovell, M.R., 2013. Tribology for scientists and engineers: From basics to advanced concepts. In: Tribology for Scientists and Engineers: From Basics to Advanced Concepts, vol. 9781461419457, Issue November. Available at: <https://doi.org/10.1007/978-1-4614-1945-7>.

surfaces at the contacting point then plastic or elastic deformation of the asperities by the load will occur. As a result the force required to overcome friction will entail the force required to shear the adhesion and to deform the obstructing asperities depending on the relative hardness of the surfaces involved (Tang *et al.*, 2008). The friction force required consist of two forces, the force to shear the adhesion of asperities and the force to elastically or plastically deform the obstructing asperities.

The value used to show the relationship between two object in contact and the normal reaction between the objects is referred to as “coefficient of friction”. The coefficient of friction of MMCs varies significantly from one another depending on a combination of many factors such as sliding speed, loading, reinforcement content and other parameters influence properties (Ceschini *et al.*, 1998). A typical example of the friction behavior of MMCs is depicted in Fig. 8 showing the variation of the friction coefficient with temperature for aluminum matrix composites. The values of the friction coefficient are initially constant until a certain temperature then there is an increase in coefficient of friction value as the temperature increases. It can be inferred that this observation is due to the softening effect of the heat on the matrix material thereby reducing the composite overall hardness. Many researchers have determined different values of friction coefficient with respect to temperature variations (Veličković *et al.*, 2016), however, some result correlate with each other while other values contradict observations of others and hence no general rule can be deduced. However, due to the high value of hardness and strength of the MMCs induced through reinforcement, the values of coefficient of friction for MMCs are relatively lower than that of metals and metal alloys.

Wear Behavior

Wear is the irreversible and progressive loss of materials during relative motion between contacting bodies (Lancaster, 1989). Due to the significant number of operating inefficiencies and economic losses in engineering assemblies sustained through this wear degradation phenomenon, extensive tribological investigations on MMCs have been carried out by various researchers (Leng *et al.*, 2009; Choi *et al.*, 2010). The general observations indicate better wear performance for MMC compared to that of materials with unreinforced matrices. During the wear test, the asperities of the unreinforced material plastically deforms hence an increase in wear while for reinforced matrices there is increased wear resistance due to the delayed plastic deformation of asperities. This is attributed to the improved strength due to the load bearing embedded particles in the composites. Some researchers have indicated that an increase in the content of the reinforcement material into the matrix can further reduce material loss through wear degradation as shown in Fig. 9. As an example, the wear rate of the Al6061 decreases as the amount of SiC reinforcing particles are added to the matrix. Baradeswaran and Elaya Perumal (2013); Tee *et al.* (2000) and Shipway *et al.* (1998) also demonstrated in their studies that there was a noticeable reduction in the wear rate as the content of reinforcing materials was increased in the composite matrix.

The effect of temperature on the wear performance of MMCs have been of significant concern. The sliding wear behavior of MMCs is important whenever relative motion is concerned. The motion can be intentional such as in the case of machining and automotive brake disks, it can also be unintentional like in the fretting wear of a joint. In some operations MMCs are exposed to tribo-contact at elevated temperatures hence the need to comprehend the thermal influence on tribological performance. Such investigations have established that there exist a critical temperature at which the coefficient of friction and the wear rate changes (Ceschini *et al.*, 1998; Tang *et al.*, 2008). Below this critical temperature the wear rate of MMCs initially decreases with an increase in temperature. After critical temperature is reached, the wear rate increases as the temperature further rises resulting in catastrophic wear (Martín *et al.*, 1996). The initial increase in wear performance can be attributed to an increase in ductility as the sample temperature is increased thereby limiting the crack formation and propagation. The extremely low wear resistance at high contact

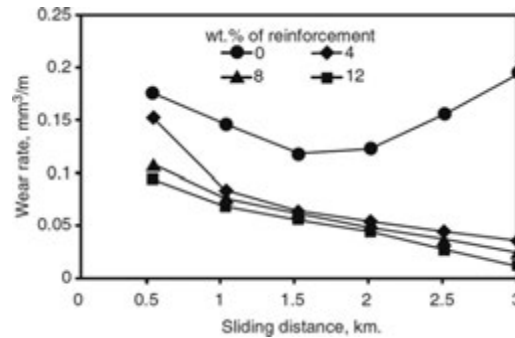


Fig. 9 Wear rate variation with sliding distance of Al6061-based MMC at sliding speed of 1.85 m/s and applied load of 10 N. Reproduced from Menezes, P.L., Ingole, S.P., Nosonovsky, M., Kailas, S.V., Lovell, M.R., 2013. Tribology for scientists and engineers: From basics to advanced concepts. In: Tribology for Scientists and Engineers: From Basics to Advanced Concepts, vol. 9781461419457, Issue November. Available at: <https://doi.org/10.1007/978-1-4614-1945-7>.

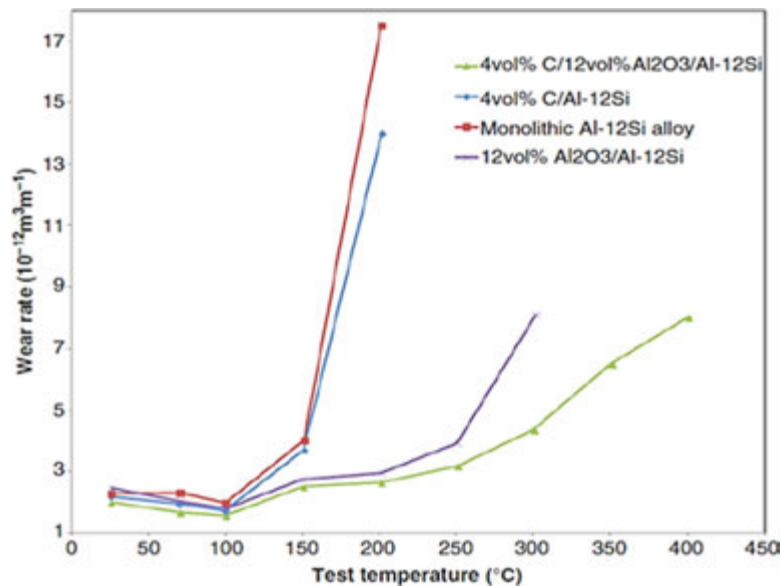


Fig. 10 Variations of the wear rate of Al based alloys with temperature. Reproduced from Menezes, P.L., Ingole, S.P., Nosonovsky, M., Kailas, S.V., Lovell, M.R., 2013. Tribology for scientists and engineers: From basics to advanced concepts. In: Tribology for Scientists and Engineers: From Basics to Advanced Concepts, vol. 9781461419457, Issue November. Available at: <https://doi.org/10.1007/978-1-4614-1945-7>.

temperatures can be expected as the material experience some degree of surface melting as well. A typical example of the wear performance behavior of MMCs is depicted in Fig. 10 showing the variation of the wear rate with temperature for aluminum matrix composites. It can also be inferred that the variation of the wear rate of MMCs with temperature is dependent on mechanical properties of the materials at high temperatures. However, some composites such as Ni-Cr-W-Fe-C-MoS₂ have self-lubricating properties at elevated temperatures due to the solid lubricating effects of molybdenum disulfide and graphite (Li and Xiong, 2008; Sun *et al.*, 2013). In such composites, at temperatures above 400°C, the graphite oxides forming a layer that complement the lubricating effect of the molybdenum sulfide thereby improving wear performance of the composite as the temperature increases.

High Temperature Thermal Properties

Specific Heat Capacity

Material selection and synthesis for high temperature applications requires scientists and engineers to understand and determine thermal properties. Heat capacity, thermal conductivity and thermal expansion are critical properties often utilized for solids such as MMCs. The heat capacity also known as the thermal capacity is a physical property of matter, defined as the amount of heat added to an object resulting in a unit change in its temperature (Almadhoni and Khan, 2015). Since the total heat a material can

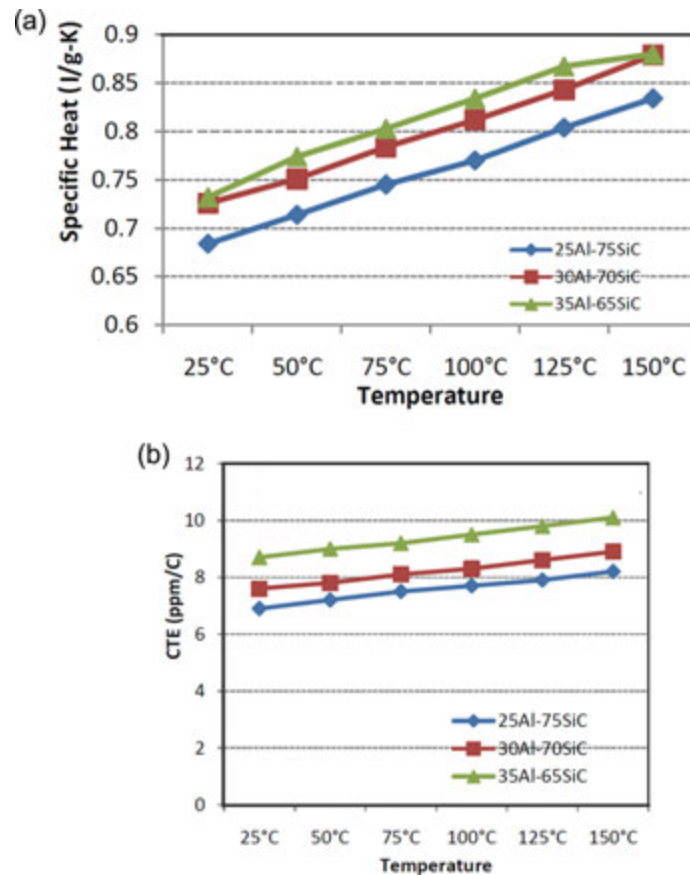


Fig. 11 Thermal properties of Al-SiC composite; (a) variation of specific heat with respect to temperature and (b) variation of CTE with respect to temperature. Reproduced from Menezes, P.L., Ingole, S.P., Nosonovsky, M., Kailas, S.V., Lovell, M.R., 2013. Tribology for scientists and engineers: From basics to advanced concepts. In: Tribology for Scientists and Engineers: From Basics to Advanced Concepts, vol. 9781461419457, Issue November. Available at: <https://doi.org/10.1007/978-1-4614-1945-7>.

absorb or dissipate is dependent on also volume or mass a parameter called specific heat defined as the heat capacity per unit mass is utilized. The specific heat of MMCs is dependent on a number of factors such as reinforcement materials, reinforcement content, matrix material and temperature of operation. For example, Fig. 11(a) shows the variation of specific heat of aluminum based MMC with respect to temperature, it shows that the specific heat capacity increases with increased temperature and with increase in the volume percentage of the aluminum reinforcement.

Thermal Expansion

Thermal expansion is the tendency of matter to experience change in volume in response to temperature variations (Vaidya and Chawla, 1994), generally materials increase volume as the temperature increases. Therefore, the thermal expansion of materials is generally expressed as fractional change in material dimensions per unit temperature change. The expansion in matter can be described in terms of Coefficient of Thermal Expansion (CTE). In MMCs the CTE is a significant parameter which influences the stability of composites at elevated temperature ranges. MMCs are highly valued for their high temperature operations and find potential applications in thermal environments such as automobile parts, brake rotors and drive shafts. These materials should have sufficient thermal stability that is to be resistant to severe geometric changes and mechanical property alterations during thermal loading. This is depicted by a graph in Fig. 11(b) showing a small increase in CTE as the temperature is increased. For greater thermal performance of MMCs, they should have lower CTE. Generally, in the absence of phase interactions the CTE of a material at a particular temperature can be expressed as:

$$CTE = \frac{\partial}{\partial T} \left(\frac{\Delta L}{L} \right) \quad (3)$$

where L represents the length of the materials and T is the temperature of the specimen. For solid material, the linear coefficient of thermal expansion $\overline{CTE}$ can be used and calculated by the formula:

$$\overline{CTE} = \frac{1}{L_0} \left(\frac{\Delta L}{\Delta T} \right) \quad (4)$$

where L_0 is the original length and ΔL is the change of length over temperature interval ΔT .

However, due to the existence of different materials within a composite, there is a high possibility of a mismatch between the CTE of the composite matrix material and the reinforcement material. The inherent thermal mismatch between the composite matrix and the reinforcement material can induce the development of residual stresses and the consequent damage or crack initiation and progression, potentially weakening the microstructural integrity and performance of composite structures (Vaidya and Chawla, 1994). Expressions for the CTE of composite with considerations of the matrix and reinforcement material stress interactions have been proposed in several investigations (Fei and Wang, 2004; Kim *et al.*, 2001; Vaidya and Chawla, 1994).

According to the Turner model, in order to analytically determine the CTE of composite materials, the following equations are to be used:

$$\alpha_c = \bar{\alpha} + V_p (1 - V_p) (\alpha_p - \alpha_m) \times \frac{K_p - K_m}{(1 - V_p) K_m + V_p K_p + \frac{3K_p K_m}{4G_m}} \quad (5)$$

Where:

$$K = \frac{E}{3(3 - \frac{E}{G})} \quad (6)$$

$$\bar{\alpha} = (1 - V_p) \alpha_m + V_p \alpha_p \quad (7)$$

where α_c represents the composite CTE, V_p is the value of the reinforcement component fractions, E and G are the longitudinal and transversal elastic modules of the matrix and the reinforcing elements, respectively.

Thermal Conductivity

Thermal conductivity of a materials is the rate at which a material transfers heat by conduction through a given unit area (Dash *et al.*, 2016). In general, the higher the thermal conductivity the higher the heat transfer rate and vice versa. Just like other thermal properties of MMCs, the thermal conductivity of a composite material depends on the operating temperature, direction of the heat flow, reinforcement volume fraction, particulate type, distribution of the reinforcements and its size. Due to the interfacial thermal barrier resistance in composites, the thermal conductivity depends on both the volume fraction of the dispersed phases as well as on the dispersion size. However, interfacial thermal barriers are expected to be effective only if they are nonparallel to the direction of heat flow. For the thermal conductivity of MMCs containing micro particles the shape and volume of the incorporated particles should be taken into consideration. Thermal boundary resistance due to the presence of pores and voids plays a significant role in lowering the thermal conductivity of composites. Furthermore, finer particles of SiC in the composite have been found to cause a considerable decline in thermal conductivity, this is because there is an increased contribution of interface to thermal resistance as particles becomes smaller.

Thermal Fatigue (Thermo-Mechanical Property)

Fundamental understanding of fatigue behavior of MMC is of great significance since they are widely featured in engineering applications that are exposed to thermal cyclic loadings due to thermal expansions and thermal contractions during service (Llorca, 2002). The main cause of thermal fatigue in MMCs is the cyclic change of temperature and complete or partial restriction of thermal deformation due to external or internal limitations, which can lead to fatigue cracking at locations with stress concentration. Generally, at elevated temperatures, the fatigue behavior of reinforced MMCs is governed by the cyclic softening and the cyclic hardening processes. The cyclic hardening process occurs through the formation and interaction of new dislocations in the matrix whereas the cyclic softening process is due to interface failure, precipitate coarsening, matrix cavitation, and the rearrangement and annihilation of dislocations (Wu and Han, 2006). At elevated temperatures MMCs mainly experience cyclic softening due to the reduction of strength in the matrix material. However, the thermal fatigue performance of the MMC can be improved by decreasing particle size and increasing the reinforcement volume fraction.

Thermal Shock Resistance

Thermal shock occurs when a material undergoing sudden changes in temperature develops internal stresses and strains that may cause cracking and eventually failure (Douin *et al.*, 2002). The resistance of MMCs to thermal shock is closely linked to its mechanical strength as shown in Eq. (8). When subjected to alternating thermal loadings, the internal stresses responsible for crack formation and propagation are formed. Under thermal loading, a material is placed under a high compression due to the high surface temperature and a large temperature gradient. This will result in viscoplastic deformations in order for the stresses to relax. Consequently, upon cooling, tensile internal stresses are generated in the composite and in turn initiate and or propagate surface cracks. Generally, materials with reinforcement demonstrate much better strength properties at elevated temperatures due to their increased thermal shock resistance (Daehn *et al.*, 1993; Ho and Saigal, 1994). In practice, thermal shock resistance is characterized

by temperature variation ΔT determined on the basis of heating and cooling cycles and expressed as follows.

$$\Delta T = \frac{\sigma(1 - \nu)}{E\alpha} \quad (8)$$

where α , σ and ν are the coefficient of thermal expansion, cracking stress and Poisson ratio respectively. The estimation of the Poisson ratio and elasticity modulus of composite can be determined using a mixing rule:

$$\nu_c = \nu_m \phi + \nu_r(1 - \phi) \quad (9)$$

$$E_c = E_m \phi + E_r(1 - \phi) \quad (10)$$

where the mean volume of fraction is denoted by ϕ , while c, m and r represent indices identifying composite, matrix and reinforcement respectively.

High Temperature Electrical Properties

Electrical Conductivity and/or Resistance

One of the important and ever-growing applications of high temperature MMCs is in electrical and electronic applications which is due to their electrical resistivities and conductivities (Chang *et al.*, 2003). However, for this application both the metal matrix and the reinforcement must have a similar CTE to minimize distortion that may arise due to mismatching thermal expansion as a result of the heating effect of current flow. One of the most used MMCs in power transmission cables is made from aluminum reinforced with alumina obeys this (Haghshenas, 2016). Electrical resistivities of MMCs are reported to be a function of the volume fraction of the reinforcement used. This behavior is mostly observed on Ag/SiC, Al/SiC, Cu/SiC and Mo/SiC composites, increasing the volume fraction of the reinforcement tends to increase the residual stresses and the dislocation density of the composite (Chang *et al.*, 2003).

Electrical conduction in MMCs is affected by the interfacial electrical resistance at the interface between the matrix and the reinforcement, this only applies if the current moves across the interface. Interfacial layer thickness heavily decreases the electrical conductivity by increasing the resistivity (William Clyne, 2017). In addition, oxide films, pores and inclusions that result from processing of the MMCs also influence the electrical conductivity of the MMCs.

Concluding Remarks

- Metal–matrix composite materials (MMCs) have been studied for two decades initially stimulated by the high performance needs of the aerospace industry. Currently, their use span across a wide range of engineering applications due to their excellent tribological properties, high mechanical properties at elevated temperatures, low coefficient of thermal expansion and high transverse stiffness.
- MMCs are characterized by low friction coefficient and excellent wear resistance compared with the unreinforced matrix due to the hardening effect of the reinforcing particles as well as the lubricating effects of solid lubrication phases such as graphite and disulfide particles.
- High temperature properties of MMCs are generally governed by the composite matrix material, reinforcement material, reinforcement volume fraction, size and distribution, operating temperature and the direction of the heat flow.
- Research into metal matrix composites is fascinating and offers endless possibilities; different matrix-reinforcement mixtures, variations of synthesis methods and parameters, reinforcement orientations and volume fractions will result in different properties, therefore the knowledge offers scientist and engineers the ability to tailor the composite for specific applications of choice.

References

- Allison, J.E., Cole, G.S., 1993. Metal–matrix composites in the automotive industry: Opportunities and challenges. *JOM* 45, 19–24.
- Almadhoni, K., Khan, S., 2015. Evaluation of the effective thermal properties of aluminum metal matrix composites reinforced by ceramic particles. *International Journal of Current Engineering and Technology* 5 (4), 2884–2897.
- Baradeswaran, A., Elaya Perumal, A., 2013. Influence of B₄C on the tribological and mechanical properties of Al7075–B₄C composites. *Composites Part B: Engineering* 54 (1), 146–152. <https://doi.org/10.1016/j.compositesb.2013.05.012>.
- Ceschini, L., Daehn, G.S., Garagnani, G.L., Martini, C., 1998. Friction and wear behavior of C⁴ Al₂O₃/Al composites under dry sliding conditions. *Wear* 216 (2), 229–238. [https://doi.org/10.1016/S0043-1648\(97\)00261-5](https://doi.org/10.1016/S0043-1648(97)00261-5).
- Chang, S.Y., Chen, C.F., Lin, S.J., Kattamis, T.Z., 2003. Electrical resistivity of metal matrix composites. *Acta Materialia* 51 (20), 6291–6302. [https://doi.org/10.1016/S1359-6454\(03\)00462-2](https://doi.org/10.1016/S1359-6454(03)00462-2).
- Choi, H.J., Lee, S.M., Bae, D.H., 2010. Wear characteristic of aluminum-based composites containing multi-walled carbon nanotubes. *Wear* 270 (1–2), 12–18. <https://doi.org/10.1016/j.wear.2010.08.024>.
- Chung, D.D.L., 2010. In: Derby, B. (Ed.), *Composite Materials: Science and Applications*, second ed. Springer-Verlag London Limited. <http://doi.org/10.1007/978-1-84882-831-5>.

- Clauer, A.H., Hansen, N., 1984. High temperature strength of oxide dispersion strengthened aluminium. *Acta Metallurgica* 32 (2), 269–278. [https://doi.org/10.1016/0001-6160\(84\)90055-5](https://doi.org/10.1016/0001-6160(84)90055-5).
- Daehn, G.S., Hebbar, K., Suh, Y.S., Zhang, H., 1993. Nonisothermal deformation behavior of a high performance aluminum matrix composite. *Composites Engineering* 3 (7–8), 699–713. [https://doi.org/10.1016/0961-9526\(93\)90092-X](https://doi.org/10.1016/0961-9526(93)90092-X).
- Dash, K., Sukumaran, S., Ray, B.C., 2016. The behaviour of aluminium matrix composites under thermal stresses. *Science and Engineering of Composite Materials* 23 (1), 1–20. <https://doi.org/10.1515/secm-2013-0185>.
- Douin, J., Donnadieu, P., Finel, A., Dirras, G.F., Silvain, J.F., 2002. Influence of the elastic stress relaxation on the microstructures and mechanical properties of metal-matrix composites. *Composites Part A: Applied Science and Manufacturing* 33 (10), 1397–1401. [https://doi.org/10.1016/S1359-835X\(02\)00155-0](https://doi.org/10.1016/S1359-835X(02)00155-0).
- Evans, H.E., Knowles, G., 1980. Threshold stress for creep in dispersion-strengthened alloys. *Metal Science* 14 (7), 262–266. <https://doi.org/10.1179/030634580790426382>.
- Fei, W.D., Wang, L.D., 2004. Thermal expansion behavior and thermal mismatch stress of aluminum matrix composite reinforced by β -eucryptite particle and aluminum borate whisker. *Materials Chemistry and Physics* 85 (2–3), 450–457. <https://doi.org/10.1016/j.matchemphys.2004.02.004>.
- Garcia-Leiva, M., Ocana, I., Martín-Meizoso, A., *et al.*, 2003. High temperature tensile and fatigue behaviour of the unidirectionally reinforced MMC Ti64/SiC. *Engineering Fracture Mechanics* 70, 2137–2148.
- Haghsheenas, M., 2016. Metal-matrix composites. In: *Reference Module in Materials Science and Materials Engineering*, pp. 1–28. Available at: <https://doi.org/10.1016/b978-0-12-803581-8.03950-3>.
- Ho, S., Saigal, A., 1994. Three-dimensional modelling of thermal residual stresses and mechanical behavior of cast SiC/Al particulate composites. *Acta Metallurgica Et Materialia* 42 (10), 3253–3262. [https://doi.org/10.1016/0956-7151\(94\)90458-8](https://doi.org/10.1016/0956-7151(94)90458-8).
- Kainer, K.U., 2006. Metal matrix composites: Custom-made materials for automotive and aerospace engineering. Kainer, Karl U. (Ed.), Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.
- Khanna, A.S., 2018. Chapter 6 – High-temperature oxidation. In: Kutz, M. (Ed.), *Handbook of Environmental Degradation of Materials*, third ed. William Andrew Publishing, pp. 117–132. <http://doi.org/10.1016/B978-0-323-52472-8.00006-X>.
- Kim, B.G., Dong, S.L., Park, S.D., 2001. Effects of thermal processing on thermal expansion coefficient of a 50 vol% SiCp/Al composite. *Materials Chemistry and Physics* 72 (1), 42–47. [https://doi.org/10.1016/S0254-0584\(01\)00306-6](https://doi.org/10.1016/S0254-0584(01)00306-6).
- Lakshmikantha, R., Auradi, V., 2020. Processing and evaluation of Al/B4C particulate MMCs: Tensile strength and wear properties under different elevated temperature test condition. *Materials Today: Proceedings* 28 (2), 504–509. <https://doi.org/10.1016/j.matpr.2019.12.209>.
- Lancaster, J.K., 1989. Fundamentals of wear. *Tribology International* 22 (4), 301–302. [https://doi.org/10.1016/0301-679X\(89\)90106-0](https://doi.org/10.1016/0301-679X(89)90106-0).
- Leng, J., Jiang, L., Wu, G., Tian, S., Chen, G., 2009. Effect of graphite particle reinforcement on dry sliding wear of SiC/Gr/Al composites. *Xiyou Jinshu Cailiao Yu Gongcheng/Rare Metal Materials and Engineering* 38 (11), 1894–1898. [https://doi.org/10.1016/s1875-5372\(10\)60059-8](https://doi.org/10.1016/s1875-5372(10)60059-8).
- Li, J.L., Xiong, D.S., 2008. Tribological properties of nickel-based self-lubricating composite at elevated temperature and counterface material selection. *Wear* 265 (3–4), 533–539. <https://doi.org/10.1016/j.wear.2007.09.005>.
- Liu, J., Fan, G., Tan, Z., *et al.*, 2019. Mechanical properties and failure mechanisms at high temperature in carbon nanotube reinforced copper matrix nanolaminated composite. *Composites Part A: Applied Science and Manufacturing* 116 (1), 54–61. <https://doi.org/10.1016/j.compositesa.2018.10.022>.
- LLorca, J., 2002. High temperature fatigue of discontinuously-reinforced metal-matrix composites. *International Journal of Fatigue* 24 (2–4), 233–240. [https://doi.org/10.1016/S0142-1123\(01\)00077-9](https://doi.org/10.1016/S0142-1123(01)00077-9).
- Macke, A., Schultz, B.F., Rohatgi, P., 2012. Metal matrix: Composites offer the automotive industry an opportunity to reduce vehicle weight, improve performance. *Advanced Materials and Processes* 170 (3), 19–23.
- Martín, A., Martínez, M.A., Llorca, J., 1996. Wear of SiC-reinforced Al-matrix composites in the temperature range 20–200°C. *Wear* 193 (2), 169–179. [https://doi.org/10.1016/0043-1648\(95\)06704-3](https://doi.org/10.1016/0043-1648(95)06704-3).
- Mohamed, F., Langdon, T., 1974. The transition from dislocation climb to viscous glide in creep of solid solution alloys. *Acta Metallurgica* 22 (6), 779–788. [https://doi.org/10.1016/0001-6160\(74\)90088-1](https://doi.org/10.1016/0001-6160(74)90088-1).
- Naplocha, K., Granat, K., 2008. Dry sliding wear of Al/Saffil/C hybrid metal matrix composites. *Wear* 265 (11–12), 1734–1740. <https://doi.org/10.1016/j.wear.2008.04.006>.
- Nturanabo, F., Leonard, M., Kirabira, J.B., 2013. Novel applications of aluminium metal matrix composites. In: Cooke, K.O. (Ed.), *Aluminium Alloys and Composites*. IntechOpen, p. 13. <http://doi.org/10.5772/intechopen.86225>.
- Ochi, Y., Masaki, K., Matsumura, T., Wadasako, M., 2004. Fatigue property and fatigue crack propagation behavior of $Al_2O_3/Al6061$ MMCs at Room and Elevated Temperature. *Key Engineering Materials* 261–263, 1073–1078. <https://doi.org/10.4028/www.scientific.net/KEM.261-263.1073>.
- Oñoro, J., Salvador, M., Cambronero, L., 2009. High-temperature mechanical properties of aluminium alloys reinforced with boron carbide particles. *Materials Science and Engineering A* 499 (1), 421–426. <https://doi.org/10.1016/j.msea.2008.09.013>.
- Peng, L.M., Zhu, S.J., 2003. Creep of metal matrix composites reinforced by combining nano-sized dispersoids with micro-sized ceramic particulates or whiskers (review). *International Journal of Materials & Product Technology, Special Issue – Microstructure and Mechanical Properties of Progressive Composite Materials* 18 (1), 215–254.
- Rashid, A., 2014. Overview of disc brakes and related phenomena – A review. *International Journal of Vehicle Noise and Vibration* 10 (4), 257. <https://doi.org/10.1504/IJNV.2014.065634>.
- Robinson, S.L., Sherby, O.D., 1969. Mechanical behavior of polycrystalline tungsten at elevated temperature. *Acta Metallurgica* 17 (2), 109–125. [https://doi.org/10.1016/0001-6160\(69\)90132-1](https://doi.org/10.1016/0001-6160(69)90132-1).
- Sherby, O.D., Burke, P.M., 1968. Mechanical behavior of crystalline solids at elevated temperature (Review). *Progress in Materials Science* 13, 323–390. [https://doi.org/10.1016/0079-6425\(68\)90024-8](https://doi.org/10.1016/0079-6425(68)90024-8).
- Sherby, O.D., Klundt, R.H., Miller, A.K., 1977. Flow stress, subgrain size, and subgrain stability at elevated temperature. *Metallurgical Transactions A* 8 (6), 843–850. <https://doi.org/10.1007/BF02661565>.
- Shin, S., Lee, D., Lee, Y.-H., *et al.*, 2019. High temperature mechanical properties and wear performance of $B_4C/Al7075$ metal matrix composites. *Metals* 9 (10), 11. <https://doi.org/10.3390/met9101108>.
- Shipway, P.H., Kennedy, A.R., Wilkes, A.J., 1998. Sliding wear behaviour of aluminium-based metal matrix composites produced by a novel liquid route. *Wear* 216 (2), 160–171. [https://doi.org/10.1016/S0043-1648\(97\)00153-1](https://doi.org/10.1016/S0043-1648(97)00153-1).
- Stojanović, B., Ivanović, L., 2015. Primjena aluminijskih hibridnih kompozita u automobilske industriji. *Tehnicki Vjesnik* 22 (1), 247–251. <https://doi.org/10.17559/TV-20130905094303>.
- Sun, J., Li, C., Tang, H., Guo, Z., Liu, J., 2013. Preparation and tribological behavior of self-lubrication composites Ni-Ni-W-Cr-Fe-Cu-MoS₂-graphite at elevated temperature. *Advanced Materials Research* 668, 3–8. <https://doi.org/10.4028/www.scientific.net/AMR.668.3>.
- Tanaka, T., Nakayama, H., Kobayashi, Y., 1996. Fatigue crack growth mechanism of MMC at room and higher temperatures. *Transactions on Engineering Sciences*. 13. <https://doi.org/10.2495/LD960201>.
- Tang, F., Wu, X., Ge, S., *et al.*, 2008. Dry sliding friction and wear properties of B_4C particulate-reinforced Al-5083 matrix composites. *Wear* 264 (7–8), 555–561. <https://doi.org/10.1016/j.wear.2007.04.006>.
- Tee, K.L., Lu, L., Lai, M.O., 2000. Wear performance of in-situ Al – TiB₂ composite, pp. 59–64.
- Thomas, A., Zervos, N., Eklund, A., Awe, S.A., 2019. Simulation study on the thermomechanical behaviour of Al-MMC automotive brake discs. In *Eurobrake 2019*. Dresden: FISITA, pp. 1–12.

- Vaidya, R.U., Chawla, K.K., 1994. Thermal expansion of metal-matrix composites. *Composites Science and Technology* 50 (1), 13–22. [https://doi.org/10.1016/0266-3538\(94\)90122-8](https://doi.org/10.1016/0266-3538(94)90122-8).
- Veličković, S., Garić, S., Stojanović, B., Venci, A., 2016. Tribological properties of aluminium matrix nanocomposites. *Applied Engineering Letters* 1 (3), 72–79.
- Verdi, D., Garrido, M.A., Múnez, C.J., Poza, P., 2017. Microscale effect of high-temperature exposition on laser clad Inconel 625-Cr₃C₂ metal matrix composite. *Journal of Alloys and Compounds* 695, 2696–2705. <https://doi.org/10.1016/j.jallcom.2016.11.185>.
- Vissutipitukul, P., Aizawa, T., 2005. Wear of plasma-nitrided aluminum alloys. *Wear* 259 (1–6), 482–489. <https://doi.org/10.1016/j.wear.2005.02.119>.
- Viswanath, A., Dieringa, H., Kumara, K.K., Pillai, U.T., Pai, B.C., 2015. Investigation on mechanical properties and creep behavior of stir cast AZ91-SiCp composites. *Journal of Magnesium and Alloys* 3 (1), 16–22. <https://doi.org/10.1016/j.jma.2015.01.001>.
- William Clyne, T., 2017. Thermal and electrical conduction in metal matrix composites. In: *Comprehensive Composite Materials II*, vol. 4. Elsevier Ltd. <http://doi.org/10.1016/B978-0-12-803581-8.09970-7>.
- Wu, C.M.L., Han, G.W., 2006. Thermal fatigue behaviour of SiCp/Al composite synthesized by metal infiltration. *Composites Part A: Applied Science and Manufacturing* 37 (11), 1858–1862. <https://doi.org/10.1016/j.compositesa.2006.01.001>.

Further Reading

- Kong, X., Wang, B., Wang, M., *et al.*, 2020. Microscratch characteristic and deformation mechanism of SiC particle-reinforced composites at elevated temperatures. *Advanced Composite Letters* 29 (1), <https://doi.org/10.1177/263336619898694>.

Creep Characteristics of Metal Matrix Composites

Hong Yang, Sarkis Gavras, and Hajo Dieringa, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

© 2021 Elsevier Inc. All rights reserved.

Nomenclature

$\dot{\epsilon}_s$ Minimum creep rate (s^{-1})
 σ Stress (MPa)
A Constant
D Diffusion coefficient
 D_{GB} Grain boundary diffusion coefficient
 D_L Lattice diffusion coefficient

G Shear modulus (MPa)
k Boltzmann constant (1.380649×10^{-23} J K $^{-1}$)
n Stress exponent
 Q_c Activation energy (J mol $^{-1}$)
R Gas constant (8.3143 J mol $^{-1}$ K $^{-1}$)
T Temperature ($^{\circ}$ C or K)
 T_m Melting temperature ($^{\circ}$ C or K)

Glossary

MMC Metal matrix composite.

MMNC Metal matrix nanocomposite.

Introduction

Creep is the plastic deformation of a material at a stress below the yield strength, at elevated temperature and over a long period of time. Elevated temperature in this case means $>0.4 T_m$, since below this temperature thermally activated deformation processes are not significant. The experimental mapping of the creep behavior of a material is carried out in creep tests in which the creep deformation is plotted as a function of the time of creep testing. The first derivative of this curve describes the creep rate. Creep tests are carried out either with tensile, compression, or shear deformation, depending on the real load case in which the material is used. Since the creep curves are recorded at a constant temperature, it should be noted that continuous sustaining of the deformation mechanisms can only be guaranteed at a constant stress. If, on the other hand, measurements are taken at a constant load, it is clear that the stress increases in the tensile creep test because the specimen cross-section decreases while it decreases in the compression creep test because the specimen cross-section increases. This changes the boundary conditions during the test and is therefore not recommended for mechanism-oriented design of experiments.

Often, but not always, creep tests show three regions. After an instantaneous deformation during the application of stress, which consists of elastic and plastic components, Phase 1 follows, in which the strain rate decreases after rapid deformation. The material undergoes strengthening in this time until a minimum strain rate is reached. This is where the second phase of the creep test begins, in which a constant deformation rate, known as the secondary creep rate, is reached. This secondary creep rate is also referred to as minimum creep rate, and here strengthening and de-strengthening processes in the material are equalized. The first two phases take place both in the tensile creep test and in the compression creep test. The third phase, in which the creep rate increases again because the de-strengthening mechanisms overtake and the sample is necked, can only be found in the tensile creep test. The third phase ends here with the failure of the sample. Only at very high stresses can such an effect occur in the compression creep test. Fig. 1 shows the typical curves of tensile and compression creep and the corresponding strain rate curves.

There is in principle an infinite number of combinations of the parameters "temperature" and "stress" for performing creep tests. This of course results in the fact that only creep tests performed at identical temperatures and stresses on two or more materials are comparable in order to answer the question of which material is more creep resistant. However, the answer then only applies to these selected parameters; at other temperatures or stresses, another material may well be more suitable for an application.

The dependence of the individual variables temperature (T) and stress (σ) is indicated in Fig. 2. With increasing temperature at constant stress or with increasing stress at constant temperature the initial deformation and the secondary creep rate increase and time to rupture decreases.

Since the secondary creep range is the dominant time span, the secondary creep rate plays an important role in the evaluation of creep tests. This secondary creep rate $\dot{\epsilon}_s$ depends on the temperature, the applied stress, and of course the tested material.

Usually, a power law describes the dependence of the minimum creep rate on the applied stress. This applies to

$$\dot{\epsilon}_s = A\sigma^n \quad (1)$$

Here, A is a temperature-dependent material constant and n is the stress exponent, which allows for estimations about the rate determining deformation mechanisms. However, since creep is a thermally activated process, just like diffusion itself, temperature dependence can be described simultaneously using an Arrhenius approach. Together with Eq. (1) this results in:

$$\dot{\epsilon}_s = A \exp\left(-\frac{Q_c}{RT}\right) \sigma^n \quad (2)$$

Here, R is the gas constant, Q_c the activation energy for creep.

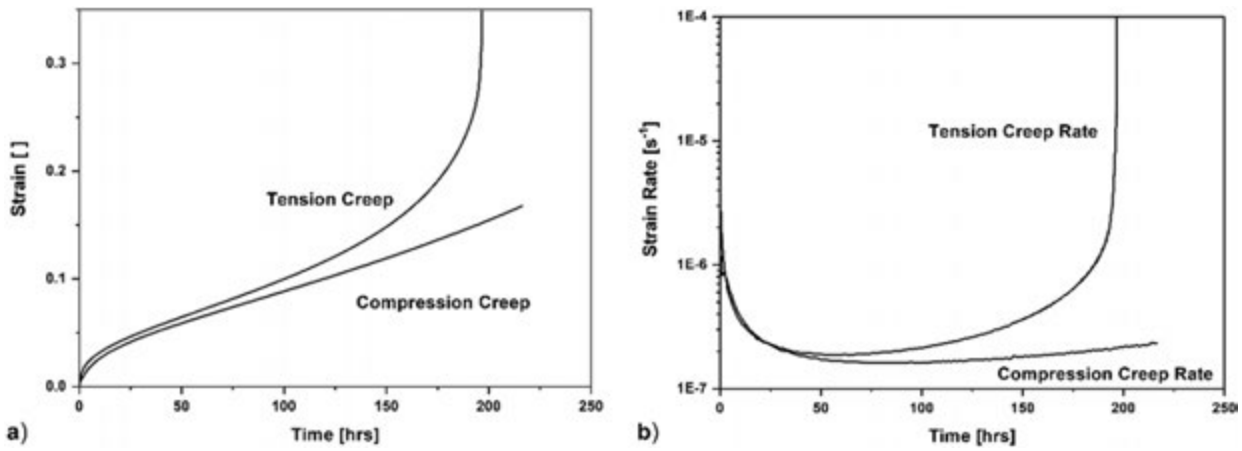


Fig. 1 (a) Examples of creep curves from tensile and compression creep tests and (b) the resulting strain rate curves.

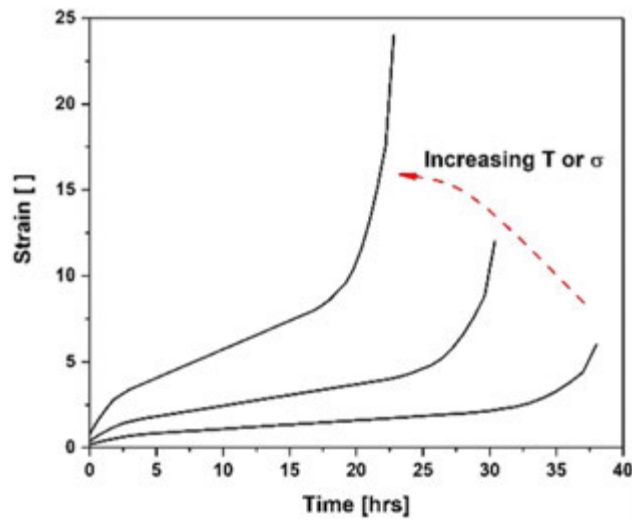


Fig. 2 Change of creep curve with increasing temperature or stress.

Different deformation mechanisms can determine the rate by which creep occurs. Their influence on the creep rate depends on the applied stress and temperature. The main mechanisms are described below.

Diffusion Controlled Creep

All deformation mechanisms can be described with the help of a strongly generalized basic equation into which the material parameters flow (Langdon, 2002). Eq. (3) represents the secondary creep rate as a function of environmental conditions and material properties.

$$\dot{\epsilon}_s = \frac{ADGb}{kT} \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad (3)$$

G is the shear modulus, b is the Burgers vector, d the mean grain diameter, k the Boltzmann constant, p and n the exponents, which are based on grain size and stress and D is the temperature-dependent diffusion coefficient:

$$D = D_0 \exp\left(\frac{-Q_c}{RT}\right) \quad (4)$$

All described simple relations can be traced back to this equation, and the following mechanisms can be represented by suitable choice of parameters in the form of this equation.

The following diffusion-based creep mechanisms are dominant when high temperatures and low stresses are acting.

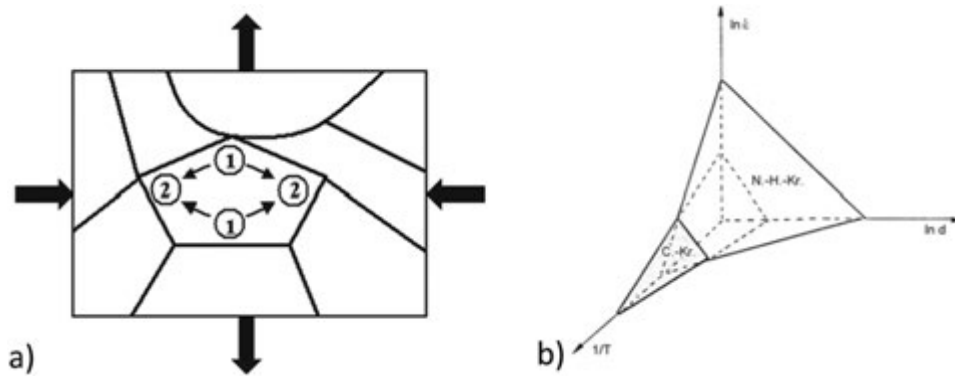


Fig. 3 (a) Schematic of the Nabarro–Herring mechanism for diffusion creep and (b) areas of the Coble (C.) and Nabarro–Herring (N.H.) creep in the opened space of temperature, creep rate, and grain size. Reproduced from Poirier, J.P., 1985. *Creep of Crystals: High-Temperature Deformation Processes in Metals, Ceramics and Minerals*. Cambridge, NY: Cambridge University Press.

Nabarro–Herring Creep

Nabarro (1948) and Herring (1950) discovered this mechanism independently of each other and established almost identical equations to describe the dependence of creep rate and stress. The model is based on the migration of vacancies as shown in Fig. 3.

Starting from a tensile load in vertical direction, the vacancy concentration is higher in the areas marked with 1 in the central grain than in the areas marked with 2. The reason for this is the grain boundary under tensile load, which thus represents a source of vacancies, since the energy required to generate a vacancy equals the amount σb^3 , where b^3 is the volume of an empty space. The grain boundaries at 2 have a formation energy increased by the amount σb^3 for a vacancy, which makes these areas vacancy sinks. The vacancies will therefore move into the areas marked with 2 (arrows). This is equivalent to an atom movement in the opposite direction and leads to an extension of the grain in the tensile direction. The model can also be applied identically to an externally applied compressive load from the side. The relationship between minimum creep rate and stress in Nabarro–Herring creep corresponds approximately to Eq. (5):

$$\dot{\epsilon}_s = \frac{ADGb}{kT} \left(\frac{b}{d}\right)^2 \left(\frac{\sigma}{G}\right) \quad (5)$$

Here $D = D_0$, i.e., the diffusion coefficient for self-diffusion in a lattice.

A first proof for the existence of the Nabarro–Herring mechanism were investigations by Weiner *et al.* (1963), in which creep investigations were carried out on an Mg-0.5Zr alloy. At temperatures of 450 and 500°C and loads of 0.76 and 1.37 MPa, areas free of Zr were visible near the grain boundaries. These areas were only at grain boundaries perpendicular to the tensile direction. A directional diffusion of the magnesium towards the grain boundaries was the explanation for the appearance of these areas.

Harris and Jones (1963) computed from the width of the resulting diffusion zones the elongation of the specimen and came to a good consistency with the theory formulated by Herring.

Coble Creep

Coble (1963) investigated the phenomenon of diffusion-controlled creep in polycrystalline material. In contrast to volume diffusion with Nabarro–Herring, the Coble mechanism is controlled by grain boundary diffusion. The creep rate in Coble creep is not dependent on the inverse square of the grain diameter, as in Nabarro–Herring creep, but on the inverse third power of the grain diameter. In Eq. (6), $D = D_{GB}$. Since the activation energy for grain boundary diffusion is (GB) smaller than for lattice or vacancy diffusion, Coble Creep occurs at lower temperatures than Nabarro–Herring creep, see Fig. 3(b).

$$\dot{\epsilon}_s = \frac{ADGb}{kT} \left(\frac{b}{d}\right)^3 \left(\frac{\sigma}{G}\right) \quad (6)$$

Harper–Dorn Creep

Harper and Dorn (1957) investigated both aluminum single crystals as well as polycrystalline aluminum in the range of low stresses close to the melting point. The result was a stress exponent of $n = 1$, but creep rates significantly higher than those to be derived from the Nabarro–Herring mechanism. In addition to this deviation from the predicted secondary creep rates, another difference became apparent. The creep rates in both the polycrystalline material and the single crystals showed virtually no dependence on grain size, which is the case in both the Nabarro–Herring and Coble mechanisms. Ardell and Lee (1986)

confirmed these results in experiments carried out on aluminum single crystals under pressure. This results in a creep mechanism that obeys Eq. (7). It is $n = 1$ and $p = 0$.

$$\dot{\epsilon}_s = \frac{ADGb}{kT} \left(\frac{\sigma}{G} \right) \quad (7)$$

Dislocation Creep

The predictions of the minimum creep rates at high temperatures and low stresses can be made with the diffusion-based descriptions mentioned above. Thus, it seems that diffusion-controlled mechanisms determine the rate of creep. At higher stresses, however, the measured minimum creep rates are higher, so further mechanisms dominating the creep rate must become effective. These are processes based on dislocation motion. Irrespective of the metal, grain size, lattice constants, lattice structure (hcp, fcc, bcc), etc., creep curves of all pure metals or alloys are very similar, which suggests that fundamental phenomena, such as strain hardening, recovery, and internal stresses, are regarded as overarching framework conditions irrespective of dislocation theories (Evans and Wilshire, 1993).

Dislocation Climb and Glide

Dislocation creep is the result of dislocations moving through the material causing plastic deformation. There are two basic types of dislocation motion, climb and glide as is depicted in Fig. 4. Weertman (1955) developed a first model in 1955 that explains a power law creep with a mechanism based on climbing dislocations. The dislocations climb over obstacles by creating and destroying vacancies.

Dislocation motion may be obstructed by precipitates, grain boundaries, other dislocations and solute in solid solution (von Buch *et al.*, 2002). Weertman assumes that the obstacles are non-mobile dislocations as described by Lomer (1951). Solute in solid solution may also slow the kinetics of dislocation motion through solute drag (Mordike, 2002; Gittus, 1974). The seminal work by Cottrell and Jaswon (1949) described that the speed of the dislocation motion is limited by the migration rate at which solute atoms glide in the slip plane and slip direction of the dislocation. It is possible, at relatively high temperatures, for dislocations to avoid those obstacles through the thermally activated process of dislocation climb (Ashby, 1972). Climb or non-conservative motion occurs perpendicularly to the direction and plane of gliding. Weertman (1957) slightly corrected the assumptions that were required for the first model and developed an extended model that could be better reconciled with measured creep rates of polycrystalline aluminum, but also describes a power law creep. The dislocations generated at Frank–Read sources accumulate at obstacles and interact with accumulations generated by other sources from parallel slip planes. If the material is exposed to a constant load, inhomogeneities occur, the compensation of which in turn leads to deformation. The creep rate is thus proportional to the number of dislocation sources N and the climbing rate of the dislocations, but inversely proportional to the distance between two adjacent accumulations of dislocations. This results in the following expression for the minimum creep rate:

$$\dot{\epsilon}_s = \frac{BD_s\sigma^{4.5}}{b^{0.5}N^{0.5}G^{3.5}kT} \quad (8)$$

The constant B is in the order of 0.2 (Lagneborg, 1972).

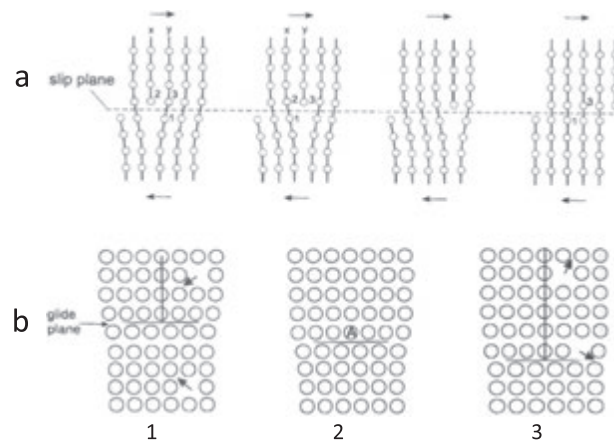


Fig. 4 (a) Dislocation glide, the arrows indicate the applied shear stress and the numbers indicate the movement of atoms, (b) dislocation climb, in (2) the dislocation is centered in row A and is shown to climb in a positive sense in (1) and negative in (3) via diffusion of atoms and vacancies. Reproduced from Hull, D., Bacon, D.J., 2001. Introduction to Dislocations, fourth ed. Butterworth-Heinemann.

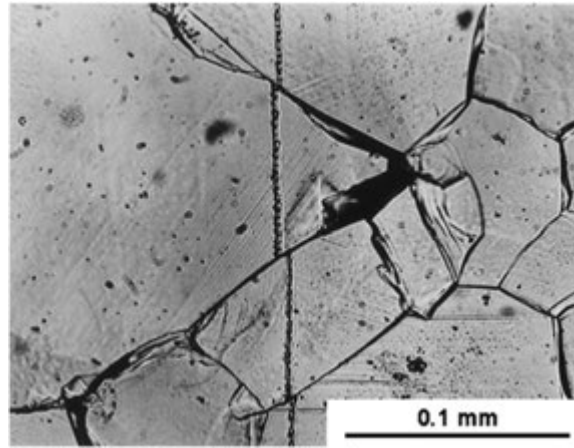


Fig. 5 Grain boundary sliding revealed through the use of a transverse marker line across grain boundaries for a Mg-0.78Al (wt%) alloy creep tested at 17.2 MPa and 200°C. Reproduced from Langdon, T.G., 2006. *Journal of Materials Science* 41, 597.

Grain Boundary Sliding (GBS)

Grain boundary sliding (GBS) is defined as the relative movement of two adjacent grains as a result of an applied stress (load) at which the movement takes place within the grain boundary or at least in its direct vicinity. This definition is taken from a review paper by T.G. Langdon, which addresses the GBS as a deformation mechanism during creep (Langdon, 2006). The two different mechanisms that can occur in GBS are explained. On the one hand there is Racher gliding, in which dislocation movement occurs within the grains, and Lifshitz gliding, which is based on diffusion processes in Nabarro and Coble creep. GBS has been observed in different metals mostly by lines scratched on a polished surface and showing a step at the grain boundaries after creep (Fig. 5).

The dependence of the deformation rate of GBS is also described. Already in 1970, Langdon (1970) formulated the dependence of the minimum creep rate being proportional to σ^2/d , resulting in the following equation, where $n = 2$, $p = 1$ and $D = D_L$.

$$\dot{\epsilon}_s = \frac{ADGb}{kT} \left(\frac{b}{d}\right)^1 \left(\frac{\sigma}{G}\right)^2 \quad (9)$$

In the following sections, methods used to help reinforce metal alloys against creep will be discussed. The methods described primarily use additional components such as particle or fiber reinforcements to help minimize the influences of the aforementioned creep mechanisms.

Creep of Particle-Reinforced MMCs

The particle-reinforced metal matrix composites (MMCs) are of importance due to their promising applications in automotive and aerospace industries at elevated temperatures (Peng and Zhu, 2003; Dieringa, 2011, 2018). The most widely used particles in MMCs are ceramic particles, such as SiC (Wang *et al.*, 2014; Aravindan *et al.*, 2015), Al_2O_3 (Hassan and Gupta, 2005; Sameer *et al.*, 2017), AlN (Saboori *et al.*, 2017), and Y_2O_3 (Han and Dunand, 2001). They are extensively utilized to enhance the matrix because of their low costs, high hardness, and high thermal stabilities at elevated temperature (Ye and Liu, 2004). These particles have the ability to improve not only the mechanical strength and ductility, but also creep resistance at elevated temperature (Goh *et al.*, 2007; Kumar and Chaudhari, 2014). According to the size of particles, the MMCs can be divided into two groups: Micro-sized particle and nano-sized particle reinforced MMCs.

Micro-Sized Particles

Labib *et al.* (2015) researched the creep properties of pure Mg and its composites with additions of 5, 7.5, 10 and 15 vol% SiC particles (10 μm) prepared by powder metallurgy and extrusion processes. The creep tests were performed under stresses ranging from 150 to 250 MPa in a temperature range of 423–473K. Fig. 6 shows that the optimum volume content of SiC particles for creep resistance in Mg alloy is 10 vol%. With further increasing content of SiC particles up to 15 vol%, there is a slight decrease in the creep resistance due to the occurrence of small clusters in the microstructure. The enhancement of the creep resistance is ascribed to the effective load transfer from the matrix to the particles and thermal mismatch between Mg matrix and reinforcements. The stress exponents of Mg and its composites are in a range of 7.0–7.9 and the activation energy values are similar to the lattice self-diffusion (92 kJ mol^{-1}), suggesting that the controlling creep mechanism could be dislocation climb by pipe diffusion.

Viswanath *et al.* (2015) studied the creep behavior of AZ91 (Mg-9.3Al-0.8Zn-0.18Mn) matrix with the reinforcements of 5, 10, 15, 20, and 25 wt% SiC particles ($\sim 23 \mu\text{m}$) at 175°C (448K) under constant stresses of 80, 100, and 120 MPa. Fig. 7 reveals that there are no obvious differences on the minimum creep rate when the content of SiC particles is below 10 wt%. However, when

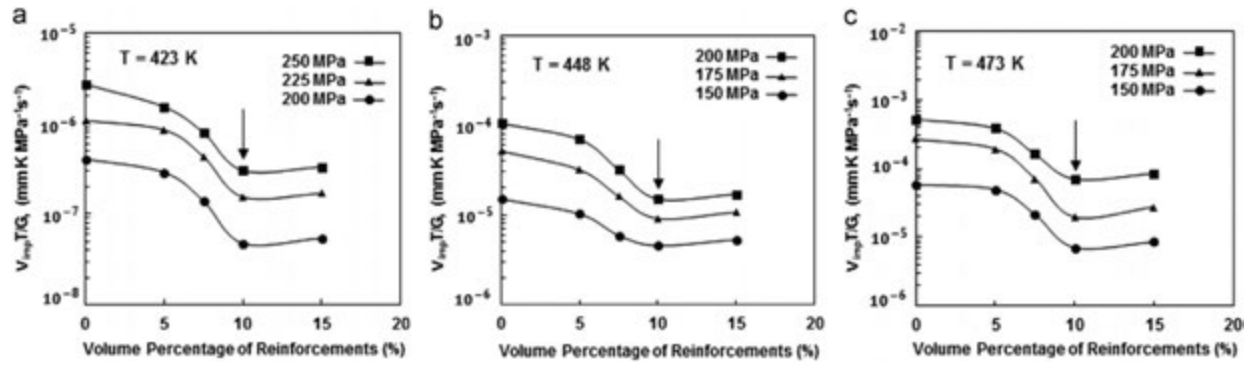


Fig. 6 Variation of normalized minimum impression velocity with vol% of particles at different punching stresses for the materials tested at (a) 423K, (b) 448K and (c) 473K. Reproduced from Labib, F., Mahmudi, R., Ghasemi, H.M., 2015. Materials Science and Engineering: A 640, 91.

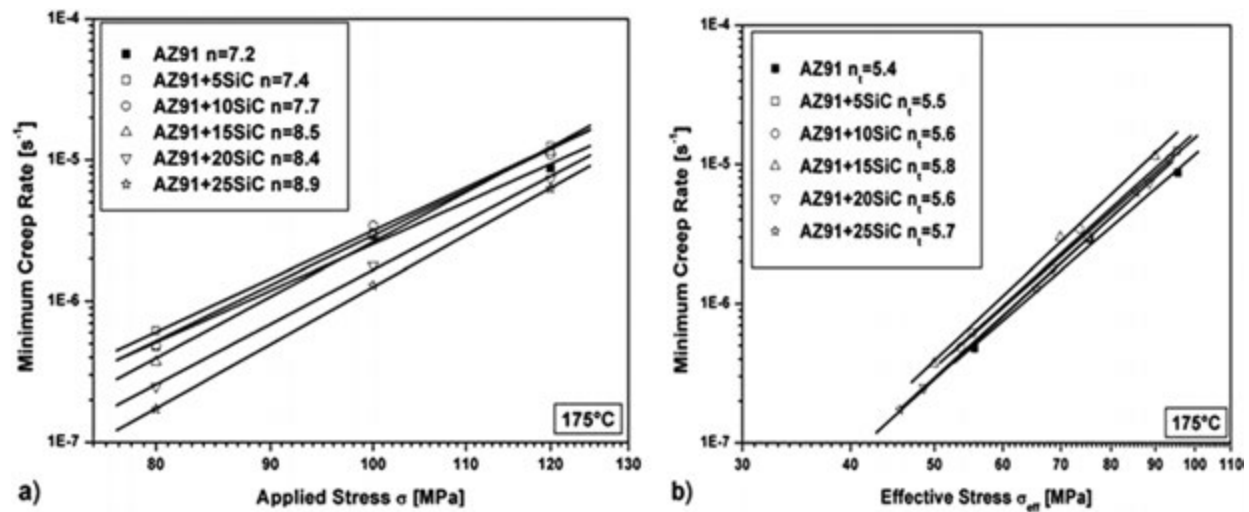


Fig. 7 Minimum creep rate vs. (a) applied stress and (b) effective stress. Reproduced from Viswanath, A., Dieringa, H., Ajith Kumar, K.K., Pillai, U.T.S., Pai, B.C., 2015. Journal of Magnesium and Alloys 3, 16.

the addition of SiC particles is up to 15 wt%, a significant improvement on the creep resistance was revealed. The true stress exponents of AZ91 and its composites were calculated in a range of 5.4–5.8, which demonstrated that the dominant creep mechanism is related to dislocation climb at elevated temperature. They suggested that the addition of hard SiC particles could impede the grain boundary sliding and the dislocation movement, which is beneficial to the creep resistance in AZ91 alloy.

It is also reported that the addition of ceramic particles could result in a decrease of the texture after extrusion (Garcés *et al.*, 2006) and thus influence the creep behavior. Garcés *et al.* (2007) fabricated Mg with the additions of 5 vol% Y_2O_3 particles (6 μm) by a powder metallurgy process and extruded at 400°C with an extrusion ratio of 20:1. Creep tests were conducted at an initial strain rate of 10^{-4} s^{-1} to reach a steady state between a temperature range of 100–500°C to obtain the stress exponent. They found that the creep resistance of unreinforced Mg is higher than reinforced Mg when the temperature is below 300°C, while its creep resistance became lower than reinforced Mg for the temperature above 300°C. For the low temperature regime (below 300°C), the creep resistance was controlled mainly by the fiber texture. It is reported that the grain orientation and ceramic particles could both contribute to the yield stress σ with this following equation:

$$\sigma_y^{comp} = A(\sigma_y)_{Tex.} + B(\sigma_y)_{Reinf} \quad (10)$$

The texture intensity for unreinforced Mg is higher than for reinforced Mg. Therefore, the creep deformation controlled by the dislocation slip is not easy to be activated in the unreinforced Mg and gives a higher creep resistance in this material. For the high temperature regime (up to 300°C), the enhancement of creep resistance from the Y_2O_3 particles became more effective in reinforced Mg, which results in a higher flow stress compared with that of unreinforced Mg.

Liao *et al.* (2010) studied the influence of T6 heat treatment on the creep resistance of Al8090 (Al81-SiCp15-Li2-Cu1.20-Mg0.80) with the addition of β -type SiC particles fabricated by spray-deposition. The creep properties were tested over a stress range of 15–150 MPa at four different temperatures (250, 300, 350, and 400°C). They found that the creep resistance of T6-aged specimen was obviously higher than that of the as-received specimen by 2–3 orders of magnitude. This is attributed to the small precipitates, that is δ' (Al_3Li)

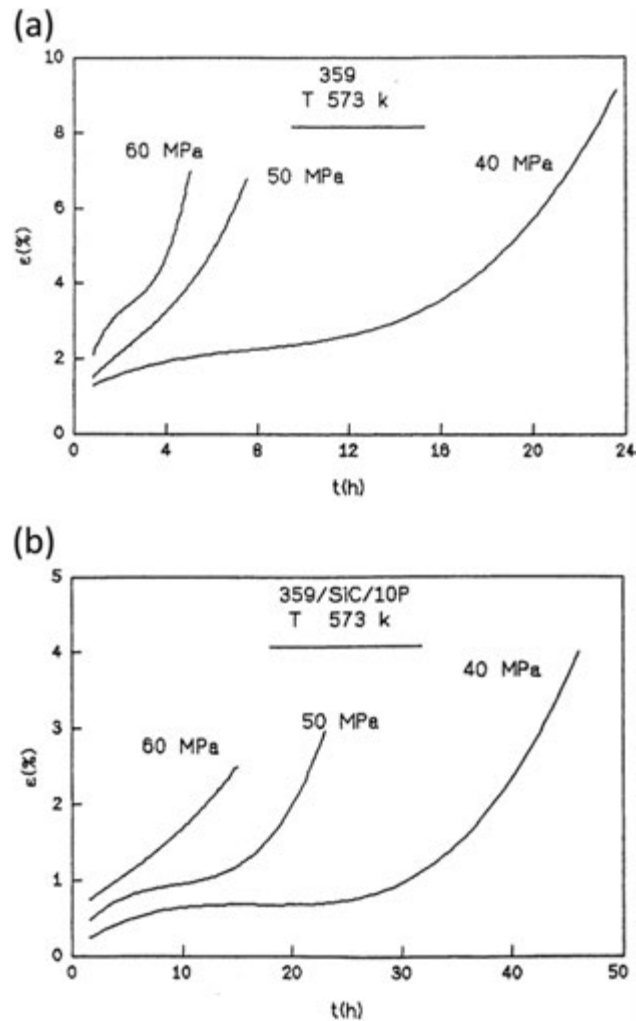


Fig. 8 The representative creep curves for (a) A359 and (b) A359/SiC/10P at 573K. Reproduced from Hamed, O.A., Shady, M., El-Desouky, A., 2001. Materials & Design 22, 473.

and S (Al_2CuMg) phases formed in the heat treated materials. They have small inter-particle spacing, which can effectively transfer the load from the matrix and enhance the creep resistance. The non-heat treated composite has a stress exponent of approximately 5. This is ascribed to the occurrence of many Cu and Mg-rich intra-granular second phases, which depletes the solid solution of these alloys. Meanwhile, the processing condition also influences the creep behavior in Al alloys, where the spray-deposited Al8090 composite has much higher creep resistance than that reported in Al2124, 6061, 7005, and 8090 prepared by powder metallurgy (PM) and liquid metallurgy (LM) methods.

The processing parameters during fabrication also influence the distribution of the particles and its creep behaviors. Hamed *et al.* (2001) added 11 vol% SiC particles with an average size of about 20 μm in Al-9Si-0.6Mg (A359) by ultrasonic stirring to study its tensile creep properties. Creep tests were conducted at 573K under different stresses between 40–60 MPa. It is found that the low melting temperature (735°C), 5 min stirring time and high solidification rate can lead to a fine dendrite arm spacing and uniform distribution of particles without any visible porosities in the composite. The formation of the Al_4C_3 phase was suppressed by the SiC particles under this processing condition. The creep curves reveal that the SiC particle-reinforced composites show better creep resistance than that of unreinforced materials under the same creep condition (Fig. 8). This is attributed to the coefficient of thermal expansion between the A359 matrix and the SiC particles, which can cause a high density of dislocations around the SiC particles during creep and increase the creep properties. They also found that the threshold stress σ_{th} decreases with increasing temperature and even disappears when the temperature is up to 750K. It is suggested that two mechanisms are related to this phenomenon: Load transfer and dislocation long range internal back stresses.

Nano-Sized Particles

It is reported that the addition of nanoparticles (NPs) could influence the formation of second phases in the matrix. Ganguly and Mondal (2018) reported on the 2.0Ca + 0.3Sb (wt%)-containing AZ91 alloy with additions of 0.5, 1.0, and 2.0 wt% SiC NPs

(average size of 50 nm) by squeeze-casting, respectively. The impression creep tests are carried out in the stress range of 300–480 MPa and a temperature range of 448–523K. They found that α -Mg, β -Mg₁₇Al₁₂, Al₂Ca, and Ca₂Sb phases were formed in the nanoparticle-free alloys. By adding SiC NPs, the formation of β -Mg₁₇Al₁₂ was suppressed while the phase fraction of Al₂Ca was increased, especially when the content of SiC NPs is 2.0 wt%. The creep rates of the composites show that the addition of SiC can effectively increase the creep resistance of a 2.0Ca + 0.3Sb (wt%)-containing AZ91 alloy and 2.0 wt% SiC shows the best creep resistance among all the materials. The stress exponents of these composites are in a range of 4.5–6.2 and the activation energies are 101.9 ± 2.5 to 115.5 ± 3.2 kJ mol⁻¹, indicating that the dominant mechanism is dislocation climb controlled by pipe diffusion during creep. This excellent creep resistance for these composites results from the increasing fraction of thermally stable Al₂Ca phase and SiC NPs, which can effectively hinder the dislocations and contribute to the superior creep resistance for the composites.

Kumar and Chaudhari (2014) studied the creep behavior on the commercially available AS41(Mg-4Al-Si) alloy with 2 and 5 wt% nano-alumina (50 nm) prepared by a combination of stir casting and ultrasonic treatment. The impression creep tests were performed at 448, 473, 498, and 523K under three constant stresses: 109.2, 124.8, and 140.4 MPa. The creep curves show that the addition of Al₂O₃ can obviously increase the creep resistance of AS41 alloy. With the increasing content of Al₂O₃ NPs, the creep resistance was increased accordingly. The calculations of stress exponents for AS41, AS41/2 wt% and AS41/5 wt% are in a range of 3–6.5, suggesting that the dislocation creep is the dominant creep deformation mechanism for AS41 and its composites. The activation energies for AS41, AS41/2 wt% and AS41/5 wt% are 66.17, 83.77, and 88.3 kJ mol⁻¹, respectively, which is close to the pipe diffusion of Mg (92 kJ mol⁻¹). They proposed that the improvement of creep resistance is ascribed to the following factors: (1) by adding nano-Al₂O₃ in AS41 alloy, the intermetallic phases were distributed evenly throughout the matrix, i.e., Mg₁₇Al₁₂ and Mg₂Si, due to the assistance of ultrasonic treatment. However, in the as-cast AS41, the intermetallics were mainly formed along the grain boundaries. (2) The strengthening effect from the nanoparticle reinforcements could also improve the creep properties of AS41 composites. Al₂O₃ NPs could (1) transfer load from matrix, (2) increase dislocation density due to the thermal expansion mismatch with the Mg matrix, and (3) hinder dislocation movement due to Orowan strengthening.

In order to investigate the effect of NPs on the creep properties in Mg-based alloys, Katsarou *et al.* (2016) fabricated the Mg-2.8Nd-1.2Gd-0.4Zr-0.3Zn (El21) alloy with and without 1 wt% AlN NPs by mechanical and ultrasound-assisted stirring. They conducted the compression creep tests at 240°C under the constant stresses range from 70 to 200 MPa. The creep curves show that its creep property was significantly improved compared with that of unreinforced El21 alloy with the addition of 1 wt% AlN NPs in El21 alloy. Its true stress exponents are in a range of 3.3–4.2, which corresponds to viscous glide of dislocation or dislocation climbing during creep. TEM characterization shows that the AlN NPs are agglomerated in the eutectic regions by the solidification front. Daudin *et al.* (2017) further studied the strengthening effect from the AlN NPs on the El21 alloy and proposed that the forest or Orowan strengthening from AlN NPs is unlikely to occur. Instead, there is an indirect influence from AlN NPs on the creep resistance. Micro-tomography characterizations display that AlN NPs can trigger the formation of dendrites in AlN-containing alloy and lead to a more branched intermetallic morphology, which may act as effective reinforcements in El21 alloy during creep (Fig. 9(b)).

Yang *et al.* (2019) fabricated the El21 alloy with 0.5 wt% AlN/Al NPs (25 wt% Al and 75 wt% AlN) with another method called high shear dispersion technique (HSDT). Creep tests were carried out at 240°C under the stresses between 70–140 MPa. It is found that the El21 + 0.5% AlN/Al NPs with the assistance of HSDT shows higher creep resistance than that of unreinforced El21 alloy (Fig. 10(a)). In particular, the HSDT plays an important role in enhancing the creep resistance of El21 alloy. El21 + 0.5% NPs sheared at 3000 rpm

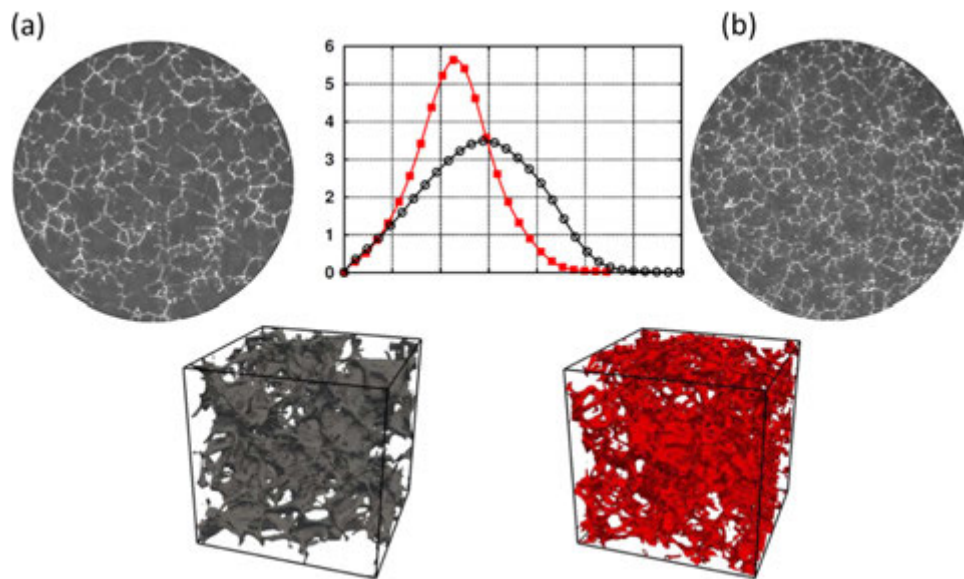


Fig. 9 Micro-tomography slice of (a) El21 and (b) El21 with AlN NPs. Reproduced from Daudin, R., Terzi, S., Mallmann, C. *et al.*, 2017. Materials Science and Engineering: A 688, 76.

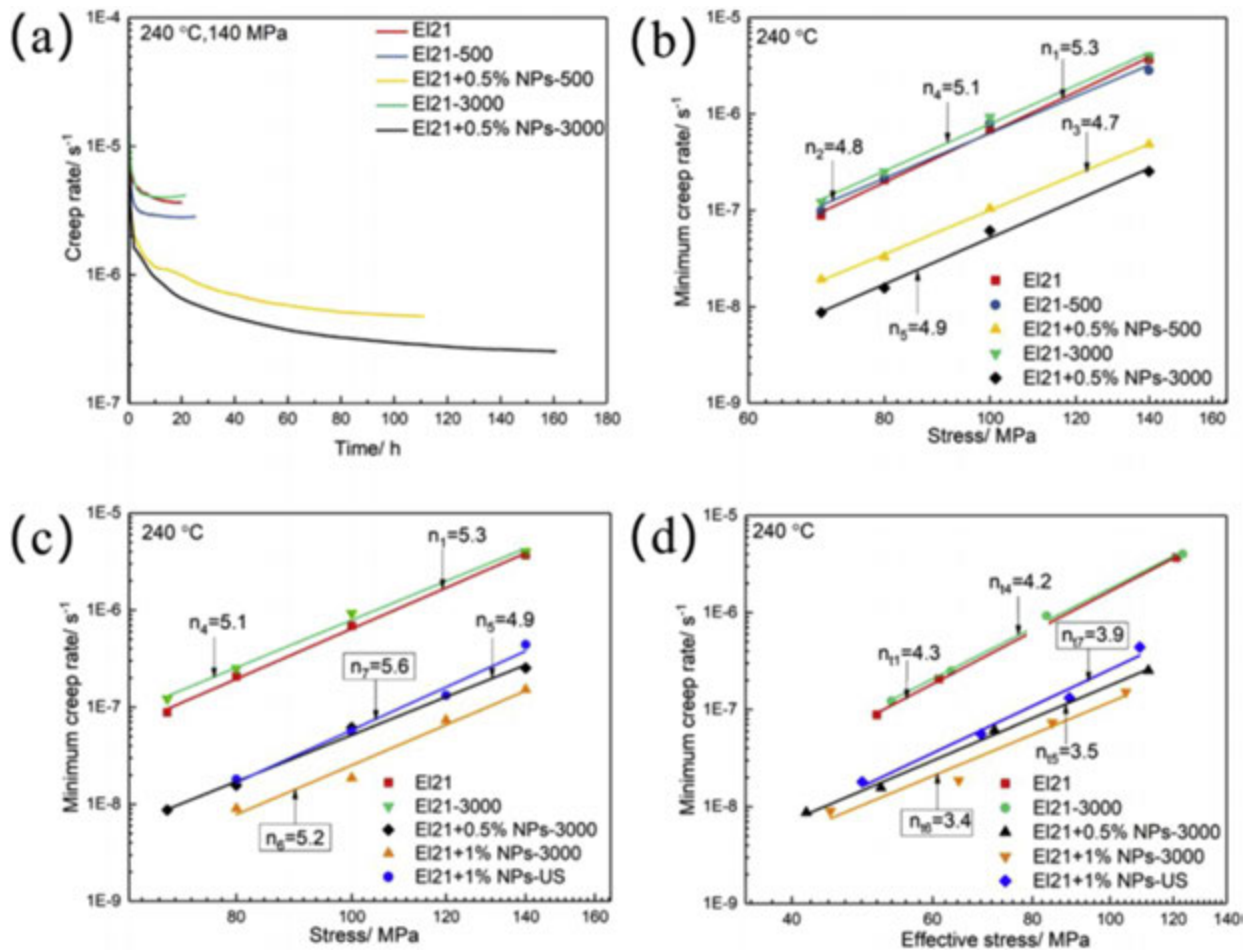


Fig. 10 (a) Creep rate vs. creep time and (b) minimum creep rate under different applied stresses for El21, El21-500, El21 + 0.5% NPs-500, El21-3000, and El21 + 0.5% NPs-3000, (c) the minimum creep rates compared with El21 + 1wt% AlN/Al prepared by ultrasonic (US) treatment and (d) the true stress exponent for all the materials. Reproduced from Yang, H., Huang, Y., Song, B., Kainer, K.U., Dieringa, H., 2019. Materials Science and Engineering: A 755, 18.

always shows lower minimum creep rate than that sheared at 500 rpm (Fig. 10(b)). Moreover, they suggested that HSDT is more effective to fabricate the NPs in El21 alloy than ultrasonic treatment in Katsarou *et al.* (2016). Fig. 10(c) shows that El21 + 1% NPs-3000 achieves a better creep resistance by HSDT than El21 + 1% NPs fabricated by ultrasonic treatment. The true stress exponent is in a range of 3.4–4.3, which is related to viscous glide of dislocation and dislocation climbing. It is concluded that the intermetallics became much thinner and more homogeneous at the grain boundaries and inside the grains, which can hinder the dislocation movement and cause the improvement on the creep resistance in AlN/Al reinforced El21 alloy (Fig. 10).

Creep of Short or Long Fiber Reinforced MMCs

Similar to micro or nano particle reinforcement, long or short fiber reinforced metals are also regarded as metal matrix composites (MMCs). The difference between long and short fibers is that long fibers may span the entire length of the cast material while short fibers are significantly shorter, on the order of 10's to 100's of microns in length. Long fiber reinforcement offers significantly higher amounts of reinforcement of the matrix compared to short fibers while short fibers are significantly easier to manufacture. However, both long and short fiber reinforced metals have been shown to have a marked improvement in the properties of the composite material.

Short Fiber Reinforced Composites

Tian and Shi (2014) showed that in an AZ91D alloy the additions of aluminum silicate ($\text{Al}_2\text{O}_3\text{-SiO}_2$) short fibers helped to improved creep resistance in comparison to AZ91D without reinforcement. The steady state creep rates of AZ91D reinforced with $\text{Al}_2\text{O}_3\text{-SiO}_2$ short fibers tested at three temperatures (473, 523, and 573K) all out performed the AZ91D alloy by at least an order of magnitude (Fig. 11). The improvement in creep properties was attributed to the load transfer from the alloy matrix to the short fibers.

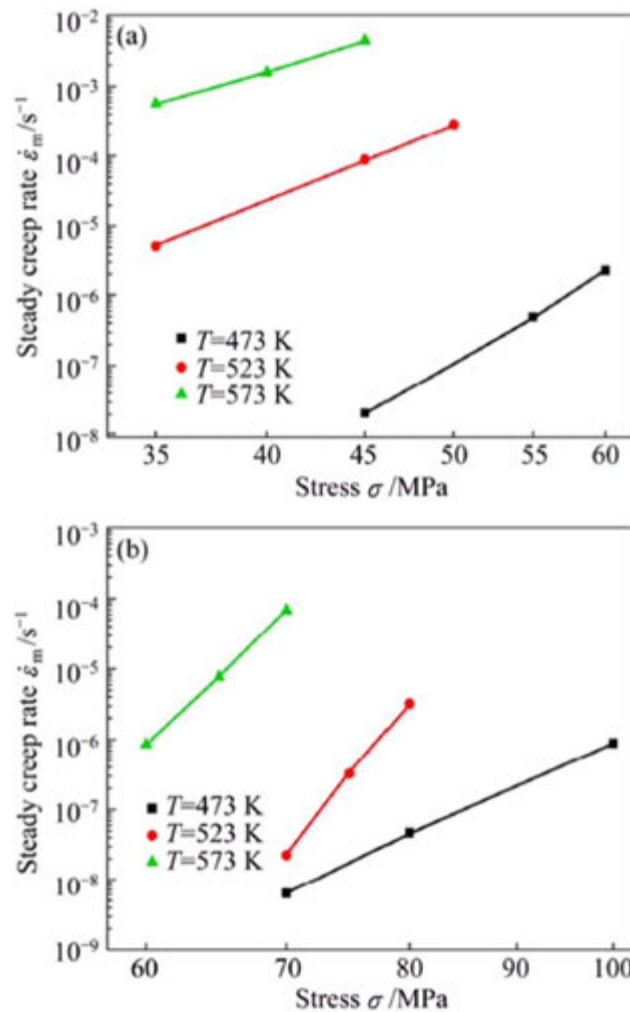


Fig. 11 Double logarithmic relationship of steady-state creep rate and stress for (a) AZ91D alloy and (b) 30% $\text{Al}_2\text{O}_3\text{-SiO}_2(\text{sf})/\text{AZ91D}$ composite. Reproduced from Tian, J., Shi, Z.-Q., 2014. Transactions of Nonferrous Metals Society of China 24, 632.

The creep stress exponent value (n) was shown by Tian and Shi (2014) to be consistent between the standard and reinforced alloys. In both cases $n = 3$, viscous slip of dislocations was the primary controller. Thus, it was concluded that creep was a function of the matrix and the short fibers present successfully acted to transfer strain out of the matrix. A similar conclusion was made by Sklenicka *et al.* (2015) in AZ91 and QE22 alloys reinforced with 20 vol% Al_2O_3 (Saffil) short fibers. A stress load transfer between the matrix and the short fiber reinforcements was shown to be the cause of the creep property improvements. Sklenicka *et al.* (2015) showed that the presence of Saffil short fibers in AZ91 reduced the minimum creep rate by 2–3 orders of magnitude (Fig. 12). The QE22 + Saffil also had improved creep properties compared to the unreinforced QE22 but only at low stresses (≤ 100 MPa). From this result, it is clear that the addition of identical concentrations of short fiber reinforcement in different alloys has a noticeable effect on the alloy's properties. Furthermore, the presence of such reinforcement can hinder other material properties. In Sklenicka *et al.* (2015), the addition of Saffil led to a significant decrease in ductility of the matrix. This resulted in the fracture of both composite alloys to be only approximately 1%–2%.

The fiber–matrix interface is a key aspect to the effectiveness of short-fiber reinforcement for creep property improvement. In a work (Dieringa *et al.*, 2005) comparing the influence of 20% Saffil short fiber reinforcements in an AE42 (Mg-4Al-2 rare earth) alloy during tensile and compression creep, microstructural investigations on the interface between fiber and matrix were shown. There was nearly no fiber pullout at the fracture surface and furthermore the matrix surface showed ductile fracture behavior (Fig. 13). As a result of this good bonding behavior between fiber and matrix, the calculated tensile threshold stress (σ_0) at 300°C and 50 MPa of AE42 + Saffil was 30 MPa. In compression creep the AE42 + Saffil achieved a σ_0 which was approximately 23 MPa higher than that of the tensile creep. These relatively good elevated temperature creep properties were again attributed to the redistribution of stress from the matrix to the reinforcement fibers.

The relative concentration of short fibers added to an alloy is also a critical parameter to maximize their positive influence on creep resistance. Requena and Degischer (2006) compared the creep behavior of unreinforced and short fiber reinforced

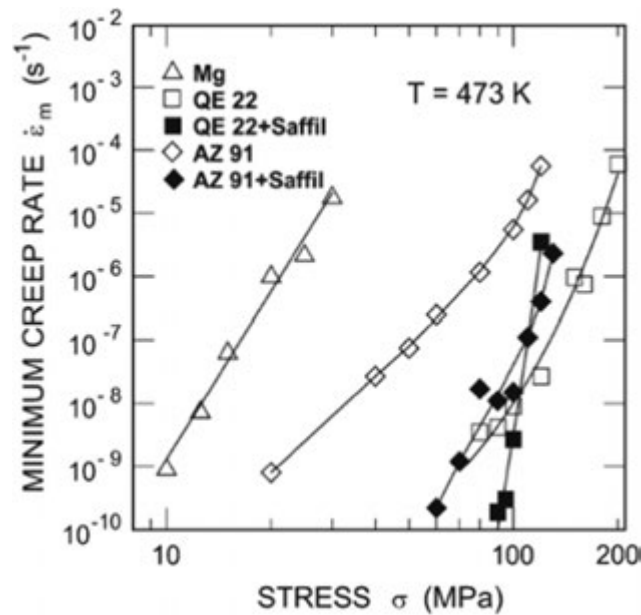


Fig. 12 Minimum creep rate vs. stress for the monolithic alloys and their short fiber composites. Reproduced from Sklenicka, V., Kucharova, K., Kvapilova, M., Svoboda, M., 2015. *Metallic Materials* 53, 221.

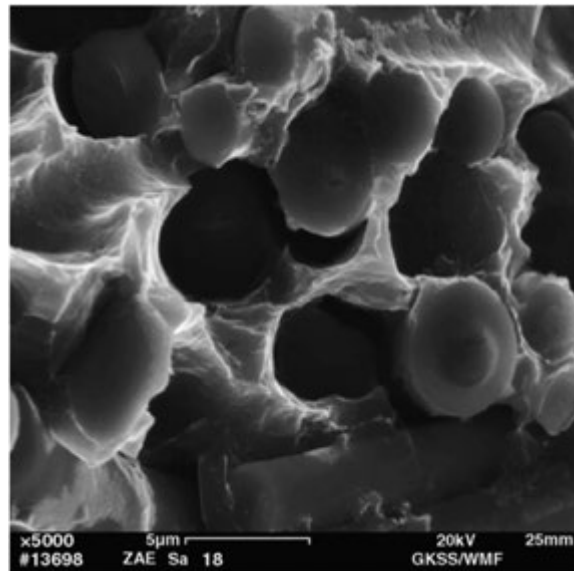


Fig. 13 SEM micrograph of a fracture surface from a tensile creep specimen tested at 300°C and 50 MPa stress. Reproduced from Dieringa, H., Huang, Y., Maier, P., Hort, N., Kainer, K.U., 2005. *Materials Science and Engineering: A* 410–411, 85.

AlSi2CuMgNi alloys. Al_2O_3 was also used as the short fiber reinforced material in concentrations of 10 and 15 vol%. During a load changing creep test, that is where the applied load and temperature during testing is varied in specific intervals, the embedding of Al_2O_3 improved the creep rate of AlSi2CuMgNi by more than one order of magnitude (Fig. 14). However, reinforcing the alloy with 15 vol% of Al_2O_3 was more effective than with 20 vol% of Al_2O_3 . This is shown in Fig. 14(a) starting at 1200 h of testing when the applied load is increased to 40 MPa. The AlSi2CuMgNi + 20 vol% of Al_2O_3 begins to go into tertiary creep. This was due to the higher defect density and greater amounts of interface area between matrix and reinforcement with approximately ≤ 1 vol% porosity. Requena and Degischer (2006) showed that the larger amounts of defects in the 20 vol% reinforced alloy accelerated the diffusion controlled creep mechanisms and the larger interface present in the material also increased the diffusivity.

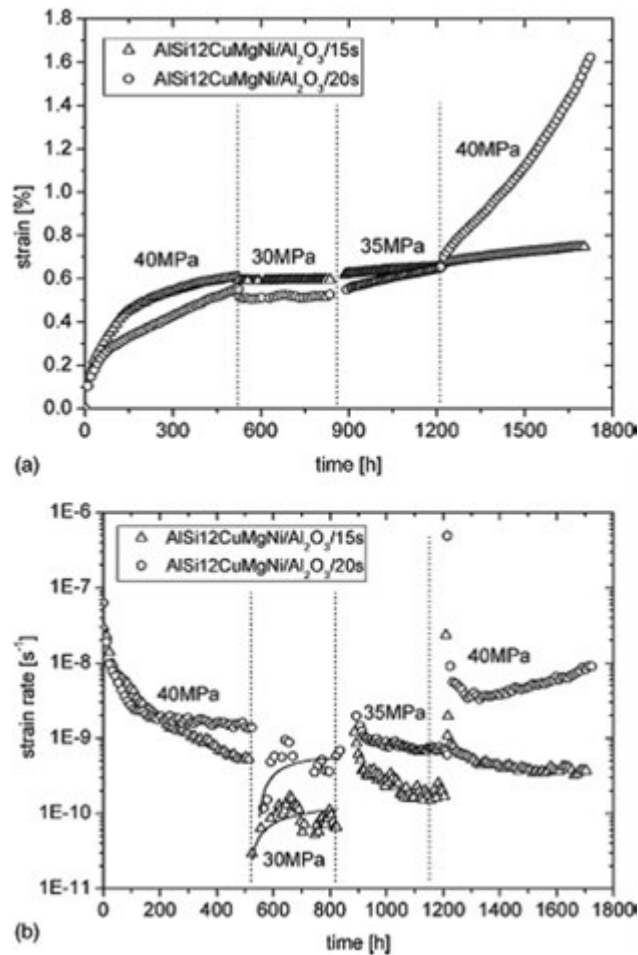


Fig. 14 A comparison of (a) strain vs. time and (b) strain rate vs. time for AlSi12CuMgNi-15 vol% Al₂O₃ and 20 vol% Al₂O₃ for a creep test sequence of 40 MPa/520 h then 30 MPa/315 h then 35 MPa/320 h then 40 MPa/510 h. Note the smaller stationary creep rate shown for the 15 vol% Al₂O₃ than for the 20 vol% Al₂O₃, which reaches the tertiary creep stage when returning to 40 MPa. Reproduced from Requena, G., Degischer, H.P., 2006. *Materials Science and Engineering: A* 420, 265.

Long Fiber Reinforced Composites

In comparison to short fiber reinforcement, there is significantly less research published on the influence of long fiber reinforcement on creep properties of light alloys such as Al alloys and in particular, Mg alloys.

Barbera *et al.* (2016) modeled interactions of fatigue and creep damage of an aluminum alloy Al2024 reinforced by Al₂O₃ long fibers which was subjected to cyclic temperature and a constant mechanical load. The different failure mechanisms which occurred such as creep ratchetting, creep-fatigue interaction, and load dwell time originated due to the difference between the fiber and surrounding matrix properties. It was found that the most significant influence to the properties of the composite was the mismatch of the thermal expansion coefficients between the matrix or the alloy and the ceramic Al₂O₃ long fibers. Micro thermal stresses would form and cause matrix micro cracks to be initiated. In order to better understand the complex interactions between matrix and reinforcement an accurate and robust direct simulation technique was utilized based on a linear matching method (LMM) framework. LMM requires a series of linear elastic solutions input parameters which are generated for discrete time points within the creep testing cycle. The values from the LMM were compared to an Abaqus simulation to further improve the understanding of the failure mechanisms in the Al2024 alloy reinforced by Al₂O₃ long fibers (Table 1).

You and Bolt (2002) compared two different matrix materials, a precipitation hardenable CuCrZr alloy and a reduced activation martensitic steel 9CrWCTa (Eurofer) reinforced by long SiC fibers. The matrix materials are used in high temperature applications as structural materials of plasma facing components in fusion reactors. As such, the long fiber reinforced composites were creep tested at 600°C and 200 MPa for Eurofer and 400°C and 200 MPa for CuCrZr. When an axial load is applied to the composites, the long-term creep rupture will occur due to the rupturing of the fibers. If a transverse load is applied, the creep rupture point of the matrix will not be significantly different to that of the long fiber reinforcements. Fig. 15 shows the creep curves of Eurofer and CuCrZr with 10 and 40 vol% SiC long fiber reinforcements under axial loading.

Table 1 Comparison between LMM and step-by-step Abaqus analyses, for different cyclic loading points

Cyclic load point	$\Delta \epsilon_p^L$		$\Delta \epsilon_c$		$\Delta \epsilon_p^{UL}$	
	LMM	Abaqus	LMM	Abaqus	LMM	Abaqus
A ₁	0.0	0.0	2.21×10^{-4}	2.53×10^{-4}	1.80×10^{-4}	2.00×10^{-4}
B ₁	2.26×10^{-3}	2.01×10^{-3}	1.76×10^{-3}	1.74×10^{-3}	3.70×10^{-3}	3.51×10^{-3}
A ₂	0.0	0.0	1.20×10^{-3}	1.25×10^{-3}	1.13×10^{-3}	1.20×10^{-3}
B ₂	5.72×10^{-3}	5.15×10^{-3}	3.22×10^{-3}	3.14×10^{-3}	8.57×10^{-3}	8.15×10^{-3}

Note: $\Delta \epsilon_p^L$ is the plastic strain increment at loading, $\Delta \epsilon_c$ is the creep strain increment, and $\Delta \epsilon_p^{UL}$ is the plastic strain increment at unloading.

Note: Chen, H., Liu, Y., 2016. International Journal of Pressure Vessels and Piping. 139–140, 159.

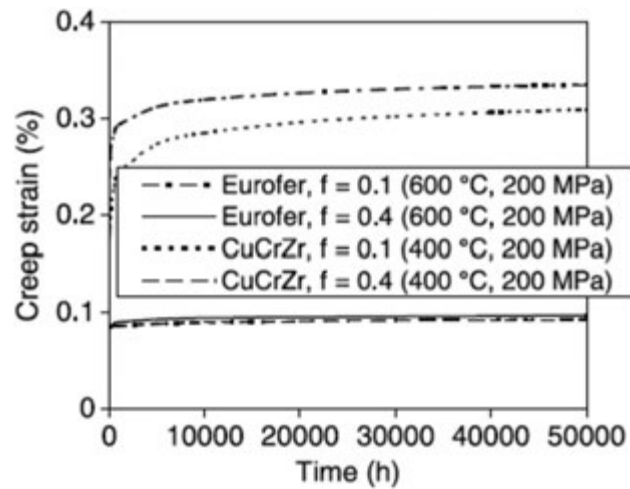


Fig. 15 Creep curves of the fiber reinforced metal matrix composites plotted for two different fibers and volume fractions. The applied stress was 200 MPa. Two different temperatures were applied to the composites: 600 °C for Eurofer and 400 °C for CuCrZr fiber reinforced metal matrix composites. Reproduced from You, J.H., Bolt, H., 2002. Journal of Nuclear Materials 305, 14.

The influence of the amount of SiC on creep strain is more apparent in Eurofer than with CuCrZr. However, in both base materials, increasing the total concentration of long fiber reinforcement improves the creep strain of the base material (Fig. 15).

Conclusions

In summary, adding ceramic particles (both micro-size and nano-sized) in MMCs is demonstrated to be an effective way to enhance the creep resistance at elevated temperatures. Based on the above, it is concluded that the creep improvement from the reinforcements in the MMCs is either by direct or indirect mechanisms (Chawla and Shen, 2001). Direct strengthening effect means there is effective load transferred from the matrix to the reinforcements. Indirect strengthening effect means the reinforcements do not effectively carry the external load directly, but strengthening the creep resistance by changing the microstructures of the matrix. One potential influence is the generation of dislocations due to the thermal expansion mismatch between the matrix and reinforcements. Another potential effect is microstructural modifications, such as the grain refinement, texture modification during deformation, and transformations of intermetallics, including composition, size, amount, morphology and distribution. These changes could probably relieve the stress concentration, hinder the grain boundary sliding and inhibit the dislocation motions, thus contributing to the creep improvement at elevated temperatures. For micro-sized particles reinforced MMCs, the amount added in the MMCs is always larger than that of nano-sized particles (above 5 vol%) (Labib et al., 2015; Viswanath et al., 2015; Garcés et al., 2007; Hamed et al., 2001). This is resultant due to the particles' relative ease to be broken up and can exhibit relatively uniform distribution in the matrix because of its lower surface to volume ratio than that of nano-sized particles reinforced MMCs. Therefore, it can be fabricated homogeneously with relatively higher volume fraction in the MMCs compared that with nano-sized particles. For nano-sized particles reinforced MMCs, its amount is normally below 5 vol% due to their poor wettability between NPs and matrix (Kumar and Chaudhari, 2014; Ganguly and Mondal, 2018; Katsarou et al., 2016; Daudin et al., 2017; Yang et al., 2019; Tian et al., 2017). It is reported that they can noticeably improve the creep response compared with larger sized counterparts (Haghshenas and Gupta, 2019; Susila et al., 2011). As was similarly concluded for MMC materials in general, for long or short fiber reinforced composites

creep properties are often improved by the transfer of load from the matrix to the fibers. This adds to the support in creep resistance given by grain boundary reinforcement, precipitation hardening, and solid solution strengthening.

However, it is still a challenge to find an effective way to distribute the NPs evenly in the matrix with higher concentrations. Therefore, achieving the balance between the size and distribution of the particles remains as a challenge and further investigations are needed in the future.

References

- Aravindan, S., Rao, P.V., Ponappa, K., 2015. *Journal of Magnesium and Alloys* 3, 52.
- Ardell, A.J., Lee, S.S., 1986. *Acta Metallurgica* 34, 2411.
- Ashby, M.F., 1972. *Acta Metallurgica* 20, 887.
- Barbera, D., Chen, H., Liu, Y., 2016. *International Journal of Pressure Vessels and Piping* 139–140, 159.
- von Buch, F., Schumann, S., Friedrich, H., *et al.*, 2002. *Magnesium Technology*. TMS. p. 61.
- Chawla, N., Shen, Y.L., 2001. *Advanced Engineering Materials* 3, 357.
- Coble, R.L., 1963. *Journal of Applied Physics* 34, 1679.
- Cottrell, A.H., Jaswon, M.A., 1949. *Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences* 199, 104.
- Daudin, R., Terzi, S., Mallmann, C., *et al.*, 2017. *Materials Science and Engineering: A* 688, 76.
- Dieringa, H., 2011. *Journal of Materials Science* 46, 289.
- Dieringa, H., 2018. *Metals* 8, 431.
- Dieringa, H., Huang, Y., Maier, P., Hort, N., Kainer, K.U., 2005. *Materials Science and Engineering: A* 410–411, 85.
- Evans, R.W., Wilshire, B., 1993. *Introduction to Creep*. Institute of Materials.
- Ganguly, S., Mondal, A.K., 2018. *Materials Science and Engineering: A* 718, 377.
- Garcés, G., Rodríguez, M., Perez, P., Adeva, P., 2006. *Materials Science and Engineering: A* 419, 357.
- Garcés, G., Rodríguez, M., Pérez, P., Adeva, P., 2007. *Composites Science and Technology* 67, 632.
- Gittus, J.H., 1974. *Acta Metallurgica* 22, 1179.
- Goh, C.S., Wei, J., Lee, L.C., Gupta, M., 2007. *Acta Materialia* 55, 5115.
- Haghshenas, M., Gupta, M., 2019. *Defence Technology* 15, 123.
- Hamed, O.A., Shady, M., El-Desouky, A., 2001. *Materials & Design* 22, 473.
- Han, B.Q., Dunand, D.C., 2001. *Materials Science and Engineering: A* 300, 235.
- Harper, J., Dorn, J.E., 1957. *Acta Metallurgica* 5, 654.
- Harris, J.E., Jones, R.B., 1963. *Journal of Nuclear Materials* 10, 360.
- Hassan, S.F., Gupta, M., 2005. *Metallurgical and Materials Transactions A* 36, 2253.
- Herring, C., 1950. *Journal of Applied Physics* 21, 437.
- Katsarou, L., Mounib, M., Lefebvre, W., *et al.*, 2016. *Materials Science and Engineering: A* 659, 84.
- Kumar, H., Chaudhari, G.P., 2014. *Materials Science and Engineering: A* 607, 435.
- Labib, F., Mahmudi, R., Ghasemi, H.M., 2015. *Materials Science and Engineering: A* 640, 91.
- Lagneborg, R., 1972. *International Metallurgical Reviews* 17, 130.
- Langdon, T.G., 1970. *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics* 22, 689.
- Langdon, T.G., 2002. *Metallurgical and Materials Transactions A* 33, 249.
- Langdon, T.G., 2006. *Journal of Materials Science* 41, 597.
- Liao, J., Tan, M.J., Sridhar, I., 2010. *Materials Science and Engineering: A* 527, 4906.
- Lomer, W.M., 1951. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* 42, 1327.
- Mordike, B.L., 2002. *Materials Science and Engineering A* 324, 103.
- Nabarro, F.R.N., 1948. *Physical Society*. 75.
- Peng, L., Zhu, S., 2003. *International Journal of Materials and Product Technology* 18, 215.
- Requena, G., Degischer, H.P., 2006. *Materials Science and Engineering: A* 420, 265.
- Saboori, A., Padovano, E., Pavese, M., Badini, C., 2017. *Materials* 11. doi:10.3390/ma11010027.
- Sameer, K.D., Suman, K.N.S., Tara, S.C., *et al.*, 2017. Microstructure, mechanical response and fractography of AZ91E/Al₂O₃ (p) nano composite fabricated by semi solid stir casting method. *Journal of Magnesium and Alloys* 5 (1), 48–55.
- Sklenicka, V., Kucharova, K., Kvapilova, M., Svoboda, M., 2015. *Metallic Materials* 53, 221.
- Susila, P., Sturm, D., Heilmaier, M., Murty, B.S., Sarma, V.S., 2011. *Materials Science and Engineering: A* 528, 4579.
- Tian, J., Shi, Z.-Q., 2014. *Transactions of Nonferrous Metals Society of China* 24, 632.
- Tian, W.-S., Zhao, Q.-L., Zhang, Q.-Q., Qiu, F., Jiang, Q.-C., 2017. *Materials Science and Engineering: A* 700, 42.
- Viswanath, A., Dieringa, H., Ajith Kumar, K.K., Pillai, U.T.S., Pai, B.C., 2015. *Journal of Magnesium and Alloys* 3, 16.
- Wang, X.J., Wang, N.Z., Wang, L.Y., *et al.*, 2014. *Materials & Design* 57, 638.
- Weertman, J., 1955. *Journal of Applied Physics* 26, 1213.
- Weertman, J., 1957. *Journal of Applied Physics* 28, 362.
- Weiner, R.T., Phillips, M., Squires, R.L., 1963. *Journal of Nuclear Materials* 8, 77.
- Yang, H., Huang, Y., Song, B., Kainer, K.U., Dieringa, H., 2019. *Materials Science and Engineering: A* 755, 18.
- Ye, H.Z., Liu, X.Y., 2004. *Journal of Materials Science* 39, 6153.
- You, J.H., Bolt, H., 2002. *Journal of Nuclear Materials* 305, 14.

Tribological Properties of Light Metal Matrix Composites

Jitendra K Katiyar, SRM Institute of Science and Technology, Chennai, Tamil Nadu, India

Jaafar Al Hammad and Abdul Samad Mohammed, King Fahd University of Petroleum and Minerals, Dhahran, Kingdom of Saudi Arabia

© 2021 Elsevier Inc. All rights reserved.

Introduction

One of the biggest challenges, engineers face during the design process, is the proper selection of materials (Nturanabo *et al.*, 2019) as some components may demand materials with conflicting properties, such as, light weight with significant strength, brittleness with excellent toughness/stiffness/fatigue resistance. Hence, to overcome these challenges, researchers in the recent past have focused on the development of composites, which gives the flexibility to engineers to select materials with the above mentioned competing properties (Nturanabo *et al.*, 2019; Donnini, 2009; Sharma *et al.*, 2020; Dhanabal *et al.*, 2015; Sujan *et al.*, 2012; Dey and Pandey, 2015; Uthayakumar *et al.*, 2012).

Composites are a mixture of two or more distinct materials, which are bonded chemically at a microscopic scale. One of the constituents of the composite material, which is continuous and available in large quantity is called as the matrix, and the other constituent, which is added to the matrix is called as a reinforcement or a filler. A metal, ceramic or a polymer maybe used as a matrix and if a metal is used then it is called as metal matrix composite (MMC). Likewise, if a polymer or ceramic is used as a matrix then it is known as a polymer matrix composite (PMC) or ceramic matrix composite (CMC), respectively. Furthermore, reinforcements or the fillers are classified based upon their shape, into several categories, such as, particulate, whisker, short/long fiber etc. (Dey and Pandey, 2015). The reinforcement in most of the cases is stronger, harder and stiffer than the matrix. The classification of composites is shown in Fig. 1.

Among the different types of composites, MMCs are the most widely used materials in many demanding applications because of their excellent properties as compared to the parent matrix material. Reinforcing a metal with different fillers has resulted in significant improvements in the mechanical properties such as the tensile strength and hardness along with an increase in their tribological performance in terms of improved wear resistance and low coefficient of friction. MMCs also have a higher working temperature, which makes them attractive for many applications. For example, the composite of aluminum/boron can retain its mechanical properties up to a temperature of 510°C, while the composition of epoxy/boron is limited to 190°C. Moreover, Aluminum/graphite and magnesium/graphite composites have also exhibited higher thermal conductivity.

It is observed from the literature that aluminum (Al) is one of the most commonly used metals in MMCs because of its high strength to weight ratio, which results in superior performance in terms of lower fuel consumption, higher thermal conductivity etc. Furthermore, molten Al has lower viscosity, which allows it to be easily used in the development of MMCs. Nowadays Mg based MMCs have also gained a lot of interest of industries because of their lightweight (two-thirds of aluminum) and good properties (AZoM, 2001; Casati and Vedani, 2014; Lim *et al.*, 2005; Gan *et al.*, 2010). Hence, the excellent mechanical and thermal properties of Al and Mg MMCs make them potential candidates for demanding tribological applications.

The aim of this chapter is to highlight the tribological behavior of light metal matrix composites in general with a special focus on Al and Mg MMCs under different operating and environmental conditions.

Tribological Behavior of MMCs

Generally, metals exhibit higher friction and wear. Therefore, to compensate for the poor tribological behavior of conventional metals, researchers have developed MMCs with improved mechanical, thermal and tribological properties. The most common wear mechanisms in MMCs during sliding are adhesive wear, abrasive wear, fatigue wear, and oxidative (corrosive) wear (Bodunrin *et al.*, 2015; Sambath and Navaneethakrishnan, 2017). Adhesive wear occurs at the interface by combination of applied load and developed shear stress, due to which cold-welding between asperities occur followed by transfer of the softer material to the hard counterpart or the pulled out particles will remain in the contact region and act as wear debris. Abrasive wear occurs when the hard asperities of the rough surface scratch or plow the softer material. For example, in ductile materials, plastic deformation takes place mainly due to the plastic follow of the softer material, while in brittle materials, wear debris entrapment takes place causing brittle fracture. Fatigue wear normally occurs under cyclic loading, resulting in a catastrophic failure, which means a sudden failure with no signs because it starts at the subsurface. Another common wear mechanism in MMCs is the oxidative wear, which takes place during sliding in a corrosive environment.

It is to be noted that, various factors, affect the tribological behavior of MMCs. They are classified into three main categories (Li and Lavernia, 2015; Panwar and Chauhan, 2018):

- (1) Properties of Reinforcement Material (volume fraction, size and shape).
- (2) Operating Conditions (normal load, sliding velocity, and sliding distance).

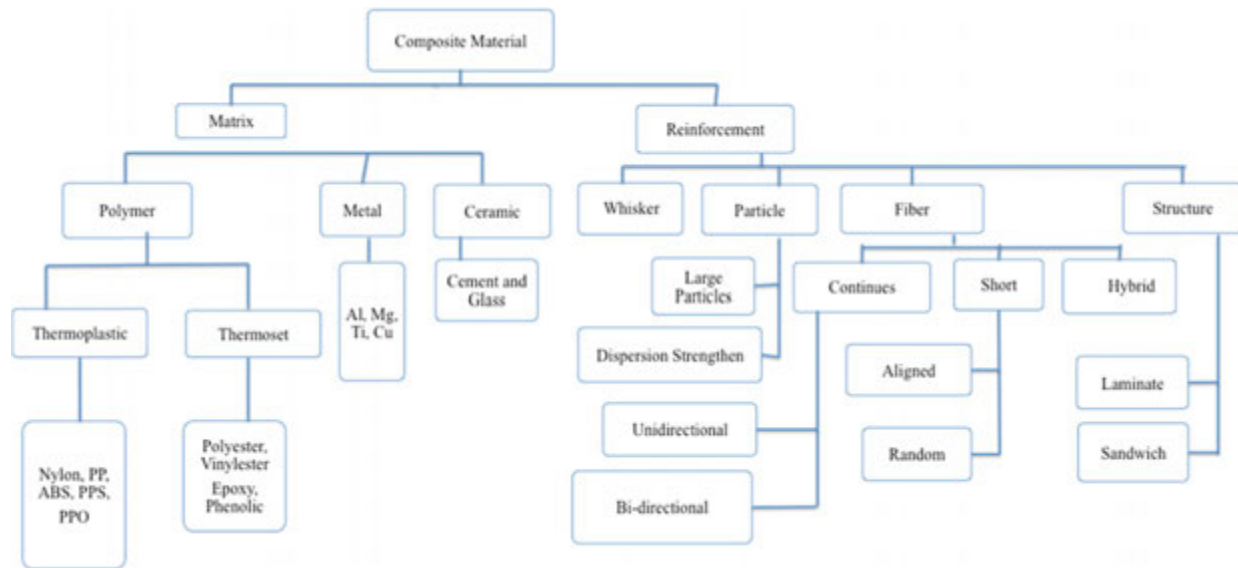


Fig. 1 Classification of Composite Materials.

(3) Environmental Conditions (temperature, relative humidity).

The effect of each of the above factors will be discussed in detail on the tribological performance of the MMCs in the following sections.

Effect of Reinforcement Volume Fraction on the Tribological Performance of Al/Mg MMCs

The volume fraction of reinforcement in the MMC, plays an important role in the enhancement of hardness of the composite. As per the Archard's wear equation, wear is inversely proportional to hardness. Hence, due to the improvement of hardness, MMCs have shown excellent wear resistance. However, to realize the full potential of these reinforcements their homogeneous dispersion in the matrix become a matter of significance. Hence, different researchers have used different fabrication techniques such as stir casting, powder metallurgy, and ultrasonic stir casting to develop MMCs with uniform dispersion of the reinforcement particles. It has been observed that the volume fraction of the reinforcement particles has shown a direct relationship to the wear resistance of composites. However, higher reinforcement content leads to the problem of agglomerations suggesting that an optimum concentration of reinforcement in the matrix is required beyond which the tribological performance is deteriorated. A reduction in wear rate of Al-MMC with an increasing volume fraction of silicon carbide (SiC) at different loads was observed (Cerit *et al.*, 2008; Choi *et al.*, 2010). Similarly, Mg-MMC reinforced with SiC has also exhibited superior wear resistance under lower loads but under higher loads it has shown higher wear rate. This was attributed to the dominance of melting at the interface due to frictional heating, which results in plastic deformation at the interface. The analysis showed that the useful load range for this composite has to be limited up to 30 N (Mondal and Kumar, 2009). Few researchers found that, beyond 20 vol%, the reinforcement did not contribute significantly to the weight loss of MMCs. Hence, they recommended a limit of 30 vol% volume fraction of the reinforcements (Cerit *et al.*, 2008; Zhang, 2008).

In an another study, wear rate and coefficient of friction of Al-MMC was found to be reduced with an increase in the volume fraction of carbon nanotubes (CNTs). However, when the volume fraction of the CNTs gradually increased beyond 4.5 vol%, the wear rate increased. The increase in wear was attributed to the formation of cracks, voids, and agglomeration of nanoparticles. A similar trend was observed for the coefficient of friction as well (Moghadam *et al.*, 2015). Moreover, no study was conducted to evaluate the tribological performance of Mg-MMCs based on different volume fractions. However, Garcés *et al.* investigated the behavior of magnesium composites reinforced with yttria (Y₂O₃) and found the effect of the volume fraction of Y₂O₃ on young modulus, and hardness, respectively. The study showed a significant increment in young modulus, hardness of the Mg-MMCs as the volume fraction of Y₂O₃ increased (Garces *et al.*, 2006). Based on this, it can be inferred that the developed Mg-MMC may show excellent tribological performance. Table 1, summarizes the studies that have been carried out by different researchers with different reinforcements to develop Al and Mg MMCs and their effect on various properties.

Hybrid metal matrix composites (HMMCs) have also reported lower wear rates as compared to only monotype of reinforcement (Mamgain *et al.*, 2015; Altinkok *et al.*, 2013; Basavarajappa *et al.*, 2006). Al-MMCs were fabricated by reinforcing aluminum with different volume fractions (10%, 15% and 20%) of two different fillers, namely, alumina (Al₂O₃) and SiC. The study reported an increase in wear resistance, impact load, and hardness of the hybrid composite by increasing the volume fraction (Mamgain *et al.*, 2015). Both adhesive as well as abrasive wear mechanisms were observed for the developed composites.

Table 1 Effect of different reinforcements on the properties of the composites

References	Composite	Fabrication process	Operating conditions	Results
(Al-maamari and Iqbal, 2019)	Al 6061/Al ₂ O ₃ and SiC	Stir casting	750°C/200 rpm/1:15 h	– Higher tensile strength. – Higher hardness and impact strength – Higher wear resistance.
(Cerit <i>et al.</i> , 2008)	AA1108/SiC	Powder metallurgy	600°C/30 min/400 MPa	– Higher hardness. – Higher wear resistance.
(Garces <i>et al.</i> , 2006)	Mg/Y ₂ O ₃	Powder metallurgy	400°C/4 h/110 rpm	– Higher modulus of elasticity. – Higher hardness
(Al-maamari and Iqbal, 2019)	Mg/Gr	Powder metallurgy	550°C/60 min/250 kN	– Low wear rate up to the optimum value of 5 wt%.
(Atthisugan <i>et al.</i> , 2017)	Mg/Gr/B ₄ C	Stir casting	800°C/700 rpm	– Low wear rate, high strength, ultimate tensile strength and wear-resistant
(Narayanasamy and Selvakumar, 2017)	Mg/Gr/MoS ₂	Powder metallurgy	530°C/60 min/740 MPa	– MoS ₂ offer better wear behavior than Gr

Table 2 Variation in the effects of volume fraction of Al₂O₃ + SiC on various properties

Composition	Impact load (Nm)	Yield strength (N/mm ²)	UTS (MPa)	Brinell hardness (GPa)
Al 6061 base alloy	5.8	125	184	60
Al 6061 + 10% (Al ₂ O ₃ + SiC)	6.9	145	270	85
Al 6061 + 15% (Al ₂ O ₃ + SiC)	7.9	300	359	105
Al 6061 + 20% (Al ₂ O ₃ + SiC)	8.7	352	415	122

Note: Mamgain, R., Manna, A., Mer, K.K.S, Chauhan, A., 2015. Effect of volume fraction (Al₂O₃ and SiC)p on the mechanical properties of Al (6061) hybrid metal matrix composite. International Journal of Scientific & Engineering Research 6 (5), 189–198.

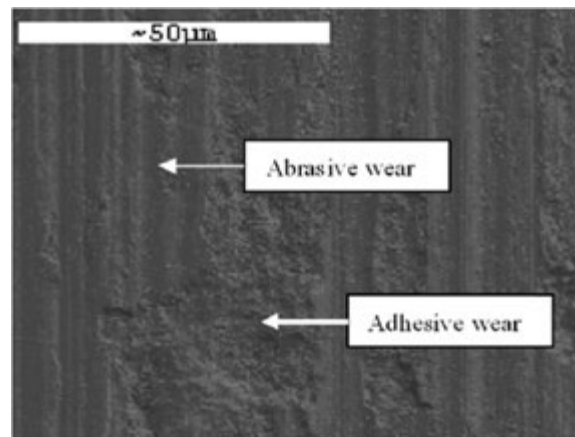


Fig. 2 SEM image showing different wear mechanisms of Al₂O₃ + SiC reinforced Al. Reproduced from Mamgain, R., Manna, A., Mer, K.K.S, Chauhan, A., 2015. Effect of volume fraction (Al₂O₃ and SiC)p on the mechanical properties of Al (6061) hybrid metal matrix composite. International Journal of Scientific & Engineering Research 6 (5), 189–198.

Furthermore, the same phenomenon was observed in other studies as well (Shil *et al.*, 2019; Rathaur *et al.*, 2019). The effects of volume fraction on various properties of Al-MMC are summarized in Table 2 Fig. 2.

Effect of Reinforcement Particle Size on the Tribological Performance of Al/Mg-MMCs

Reinforcement particles size is another important factor, which significantly affects the mechanical and tribological properties such as hardness, wear resistance, and friction coefficient. It is observed that the nano range particles exhibit excellent wear resistance property as compared to micron size particles (Shinda *et al.*, 2020). Tribological studies were carried out on Mg-MMCs reinforced

Table 3 Variation of different particle size on Al, Mg, and hybrid reinforcement

References	Matrix	Fabrication process	Reinforcement details		Operating conditions Load (N); speed (m/s); sliding distance (m)	Results
			Reinforcement	Size; wt%		
Al composites (Goudarzia and Mohammad)	Al5252	PM	SiC	60 μm ; 2.5–10 wt%	15–45; 0.5; 1000	Similar results between base material and reinforced composites at lower loads. Nano composites showed lower wear rate than micro composites at higher loads. COF of nano composites are lower than micro composites.
(Hosseini <i>et al.</i> , 2010)	Al6061	PM	Al_2O_3	30 nm 1 μm 60 μm	20; 0.08; 1000	Lower density and hardness as particle size increase. Higher wear rate as particle size increase.
(Nieto <i>et al.</i> , 2017)	AA5083	CrM & DMDF	B_4C	40 nm; 5 vol% 0.5 μm ; 5 vol% 1–7 μm ; 5 vol%	133.4; 2000 rev; 1436	Abrasion is the predominant wear mechanism. Interaction of B_4C , result in higher hardness. Better bonding for smaller particle sizes. Higher hardness resulted in elevated wear resistance of nano composites.
Mg composites (Hassan, 2006)	Mg	PM and DMD	$\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$, and ZrO_2	Nano; 0.66 vol% 0.3 μm ; 0.66 vol% 1 μm ; 0.66 vol%	150,000; 500°C; 12 h	Higher yield strength, and ductility as particle size is reduced. Superior improvement in fracture resistance for smaller particle size.

Abbreviations: Al, aluminum; Al_2O_3 , aluminum oxide; B_4C , boron carbide; B.A, bagasse ash; DMD, disintegrated melt deposition, CrM & DMDF; forging process; PM, powder metallurgy; SiC, silicon carbide; S.C, stir casting.

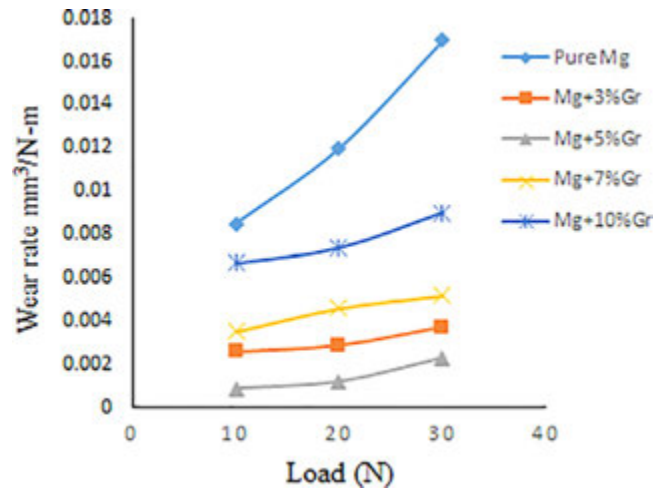


Fig. 3 Variation of wear rate with varying applied load of Mg matrix. Reproduced from Al-maamari, A.E., Iqbal, A.A., 2019. Wear and mechanical characteristics of Mg-Gr self-lubricating composite fabricated by mechanical alloying. *Journal of Magnesium and Alloys* 7 (2), 283–290.

with SiC_p (Zhang *et al.*, 2008). It was observed that as a result of increasing particle size of SiC_p , wear rate of the Mg-MMC increased. However, some studies have also shown a different pattern in which the wear rate of the composite varied considerably with increasing particle size. The study of aluminum composite reinforced by SiC_p illustrates this exception. It is clearly observed that the wear rate of the composite initially decreased with increasing particle size from 2 to 20 μm but a further increase in the particle size, the wear rate increased significantly. It is concluded that an optimum range of particle size is needed for better tribological properties.

Particle size also has an effect on the coefficient of friction of the composites. Studies were conducted to evaluate the wear rate and coefficient of friction of Al-MMC reinforced by 15 vol% of nano and micro sized Al_2O_3 particles. It was concluded that wear rate and coefficient of friction of the aluminum composite increased with an increase in the particle size of alumina (Jan *et al.*, 2006; Yashpala *et al.*, 2020). Further, the obtained results from the various studies are summarized in Table 3.

Effect of Operating Conditions on the Tribological Performance of Al/Mg-MMCs

It is to be noted that the tribological response of any material is not an intrinsic material property but it is a system's response. Thus, the tribological properties of any material in general are dependent upon the operating and environmental conditions. Therefore, it is necessary to discuss the affect of the operating conditions such as, normal load and sliding speed on the tribological properties of MMCs.

Effect of normal load

It is observed that normal load adversely affects the tribological performance of the MMCs. As the normal load increases, fracture of the reinforcement particles may happen due to an increase in higher contact pressures which further results in higher wear of materials (Al-maamari and Iqbal, 2019). The study of pure magnesium reinforced by different volume fractions (3, 5, 7, 10 vol%) of graphite (Gr) under different normal loads is illustrated in Fig. 3, which was conducted on a pin-on-disk tribometer. It was concluded that as the load increased the wear rate increased for all the compositions. However, the composite of Mg- 5 vol% Gr showed the best tribological performance in terms of lowest wear rate and coefficient of friction. As the volume fraction of graphite exceeded 5 vol%, both, wear rate and friction coefficient increased because of the formation of wear debris. It is also observed that oxidative wear was the predominant wear mechanism at higher loads and adhesive wear was predominant at lower loads (Wilson and Alpas, 1996; Gul and Acilar, 2004). Lim *et al.* (1997) analysed the friction and wear behavior of Al-Cu alloy with graphite particulates. They found a flaky layer of graphite at the counterface due to which, the metal to metal contact reduced, resulting in lower friction coefficient and improved wear resistance. This can be clearly seen in Fig. 4, which exposed that the wear rate increases with increase in applied load for all specimens. In another study, (Lim *et al.*, 2003) reported that magnesium metal matrix composite with interconnected galvanized iron (5 vol%) shows improved mechanical properties such as stiffness and hardness as compared to pure magnesium. They also evaluated the tribological properties of Mg MMCs using a pin-on-disc tribometer at different normal loads ranging from 4 to 30 N and at a sliding speed of 1 m/s. They observed that reinforced composite showed improved wear resistance by a magnitude of 2.7 times that of pure magnesium. Manoj Kumar *et al.* (2005) reinforced magnesium matrix with SiC_p and evaluated the fretting wear of the composites. They reported that abrasive wear was most dominant wear mechanism at the interface, which reduced due to the formation of hydrated magnesium silicate as schematically described in Fig. 5.

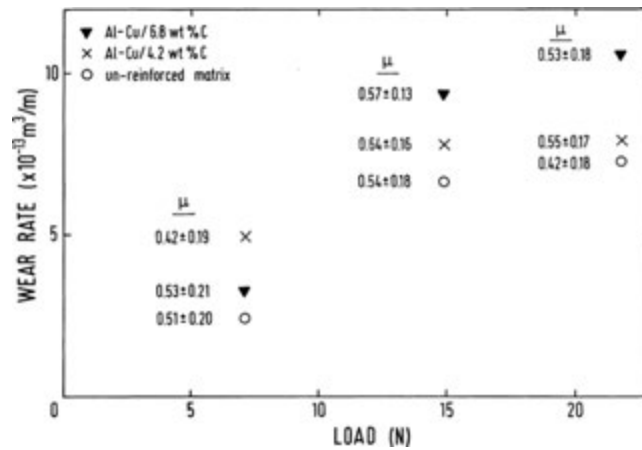


Fig. 4 The variation of wear rate with applied load. Reproduced from Lim, S.C., Gupta M., Ng W.B., 1997. Friction and wear characteristics of Al-Cu/C composites synthesized using liquid phase casting process. *Materials and Design* 18 (3), 161–166.

Selvam *et al.* (2014) evaluated the tribological properties of Mg MMC reinforced with ZnO nano particles. They conducted the wear tests at normal loads of 5–10 N, and sliding speeds of 0.6–1.2 m/s for sliding distances of 500, 1000 and 1500 m, respectively. It was observed that wear rate increases with an increment in sliding speed with two different slopes as shown in Fig. 6. Initial slope is observed due to the formation of grooved, scratches and wear-debris and second slope is because of the formation of oxide layer at higher speed. However, a decrement in friction coefficient was observed with increase in sliding distance. Iruthaya Raj *et al.* (2019) added molybdenum nanoparticles in Mg MMC for improvement in tribological properties and mechanical properties. They performed the tribotest on a pin-on-disc tribometer at 1.25 m/s sliding speed and varying applied loads from 5 to 25 N for a sliding distance of 1000 m. A decrease in the wear rate of the composite was observed with an increase in the concentration of molybdenum at all loads as shown in Fig. 7.

Uthayakumar *et al.* (2012) developed a hybrid metal matrix of Al reinforced by 5 vol% of SiC and 5 vol% of B₄C and evaluated its tribological properties using a pin-on-disc test. Wear and coefficient of friction were evaluated under varying loads between 20 and 100 N at different sliding velocities. The investigation showed high friction coefficient for unreinforced aluminum, while a low coefficient of friction for the reinforced matrix with a critical load point of 60 N. The reduction in the friction coefficient was attributed to the generation of boron oxide layer at the contact zone due to the frictional heat. Increasing the load beyond the critical point caused the coefficient of friction to increase due to the rupture of the oxide layer. Another investigation was conducted on a composite of Al reinforced by B₄C, which exhibited a critical load point of 65 N. It is concluded that the ceramic particles, which are embedded in the Al matrix, reduced the plastic deformation. As it is known that, Al is environmentally reactant and forms an oxide layer during sliding. The formed oxide layer reduces the contact between surfaces, and the pull out of these particles is very low at lower loads. However, once the load increases beyond a critical point, the pull out increases due to the tearing of the oxide layer due to which large amount of wear debris are generated. The large generation of debris indicates severe plastic deformation. Same effect was observed in a study on Al reinforced by SiC (Alpas and Zhang, 1992; Natarajan *et al.*, 2006). Table 4 gives a summarized view of the effect of load on the tribological properties of MMCs for an easy understanding.

Effect of sliding speed

Sliding speed is another important factor, which affects the tribological behavior of MMCs. From the previous studies it is observed that the sliding speed has a direct proportionality with wear rate. In other words, increasing the sliding velocity increases the wear rate. The effect of sliding speed does not only stop on increasing wear rate, but it also increases the temperature at the interface between the surfaces, resulting in the softening of the matrix, increased rate of oxidation, and a reduction in material flow stress. As a result, the sliding velocity might have different effects on the MMCs with different materials (Natarajan *et al.*, 2006). Further, the effect of sliding speed on wear rate of aluminum reinforced by different weight percentages (2.5, 5 and 7.5) of MoS₂ and 10 wt% of B₄C have illustrated by Monikandan *et al.* (2016). The addition of MoS₂ and B₄C enhanced the hardness and fracture toughness of the composite. The addition of MoS₂ aided in the formation of a lubricated layer that reduces the wear rate and friction coefficient. However, when the sliding velocity increased beyond 2 m/s, wear rate and coefficient of friction gradually increased due to a rise in temperature resulting in the evaporation of the lubricated layer leading in metal-to-metal contact (Monikandan *et al.*, 2016).

Weia *et al.* (2013) investigated the tribological properties of Mg MMC reinforced with SiC and MWCNTs at different sliding velocities. It was observed that the addition of SiC and MWCNTs tends to increase the specific wear rate at a low sliding velocity of 1.5 m/s. while for higher velocities, specific wear rate decreased gradually up to 3.5 m/s. A combination of abrasion and oxidation wear mechanisms were found to be responsible for higher wear rates a sliding velocity below 1.5 m/s. Once the velocity goes beyond 1.5 m/s, the wear at the grooves, which were formed at low speed are transformed to scratches followed by plastic deformation causing a drop of the wear rate. The drop is related to the increase in flash temperature due to the increase in the

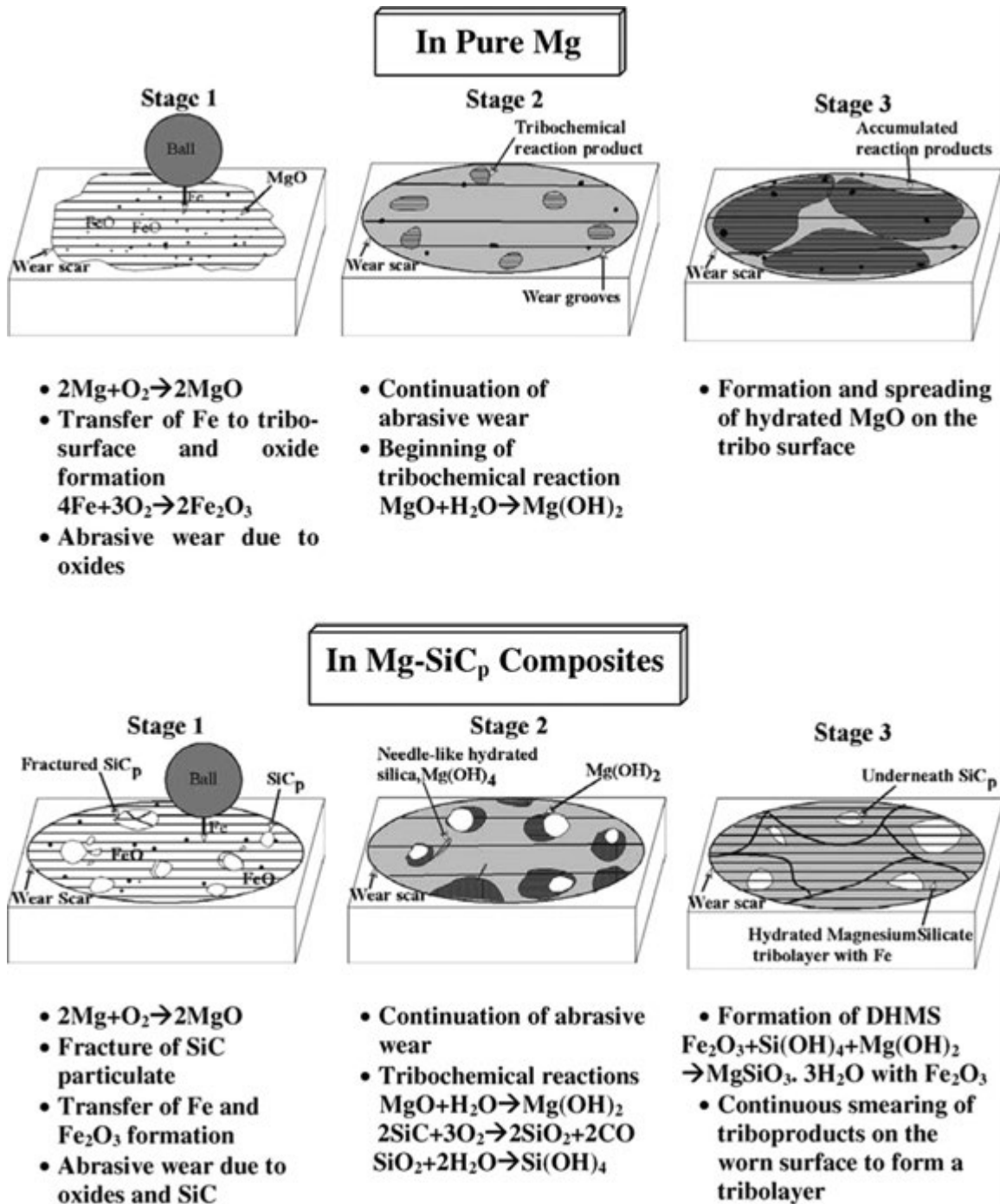


Fig. 5 Schematic representations of wear mechanisms during tribotest. Reproduced from Manoj Kumar, B.V., Basu, B., Murthy, V.S.R., Gupta, M., 2005. The role of tribochemistry on fretting wear of Mg-SiC particulate composites. Composites – Part A, 36, 13–23.

sliding velocity causing softening of the mating surfaces in which the lowest wear rate was recorded at 3.5 m/s. Another investigation shows similar behavior in which at higher speeds, wear is transformed from cutting to plowing where the removed materials are displaced. As a result of that, the use of SiC and MWCNTs appears to be more beneficial when used at higher speeds in which wear rate decreases. It was observed that the removal rate of the oxide layer rate is higher during sliding as compared to the rate of formation (Weia *et al.*, 2013; Lim *et al.*, 2005). Shanthi *et al.* (2010) reinforced AZ31B magnesium alloy matrix with aluminum oxide with/without calcium and investigated its tribological performance under different conditions. They observed that the composite showed abrasive wear at lower speeds and adhesive wear at higher speeds. At higher speeds, the thermal softening played a very important role in the reduction of friction coefficient and wear resistance (up to 30%), which can be clearly

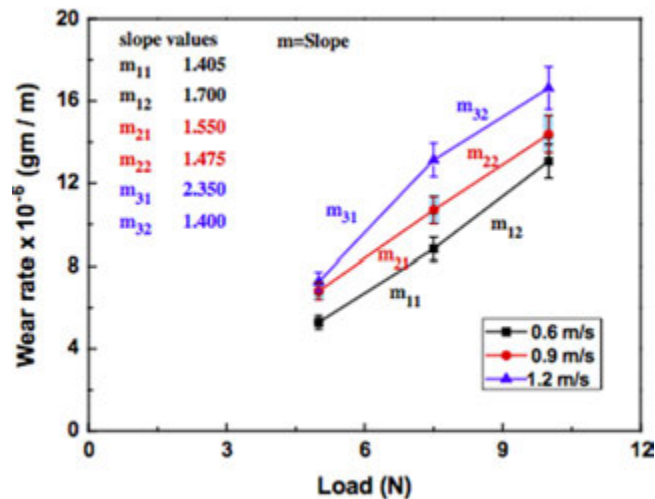


Fig. 6 Wear rate with respect to applied load at various sliding speed. Reproduced from Selvam, B., Marimuthu, P., Narayanasamy, R., *et al.*, 2014. Dry sliding wear behavior of zinc oxide reinforced magnesium matrix nano-composites. *Materials and Design* 58, 475–481.

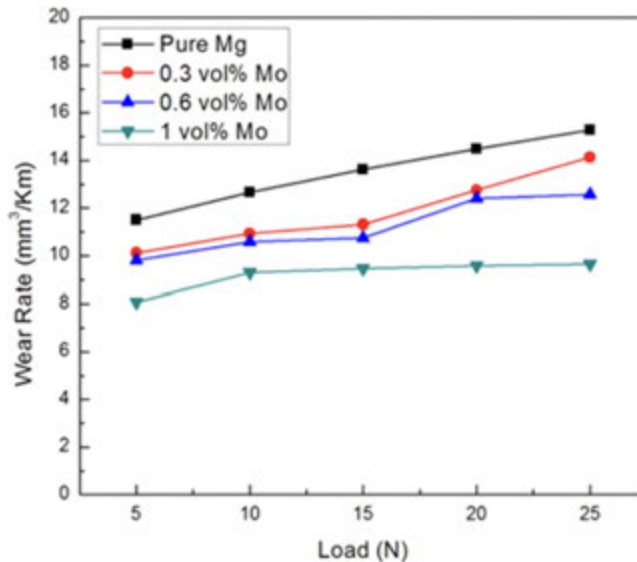


Fig. 7 Effect of applied load on wear rate. Reproduced from Iruthaya Raj, M.J., Manisekar, K., Gupta, M., 2019. Mechanical and Wear Properties of Mg/Mo Nanocomposites. *Kovove Materialy-Metallic Materials* 57, 237–246.

observed from Fig. 8. (Srinivasan *et al.*, 2012) developed AZ31B and nano composites (AZ31B- Al_2O_3 -Ca) using hybrid-casting process followed by hot extrusion. Pin-on-disc wear tests were conducted for a sliding distance of 2000 m at a normal load of 10 N at different sliding speeds, ranging from 0.6 to 1.2 m/s at room temperature. They also observed similar behavior that the wear decreases with an increase in sliding speed and observed plowing groove, adhesion and oxidation to be dominant wear mechanisms followed by thermal softening at higher speeds. Table 5 presents a summarized view of the different studies showing the effect of sliding speed on the tribological properties of Al and Mg MMCs.

Effect of temperature

Temperature is another important factor that affects the wear behavior of the composites, which results from the increase in the sliding velocity, and load as discussed in earlier sections. Poor strength and bonding at high temperatures are the main problems that sidelined magnesium and aluminum for demanding applications, and the effective approach to overcome this is adding reinforcement with the matrix to enhance its mechanical properties at higher temperatures. Some studies reported that the addition of reinforcement is beneficial only at lower loads and temperatures (Labib *et al.*, 2016). A study was conducted on Al6061 and Al A356 reinforced by SiC, Al_2O_3 , and graphite, respectively. The effect of ceramics and graphite were tested under specified operating conditions of low load (11.55 N), and low sliding velocity (0.1 m/s). Effect of reinforcements is shown in Table 6. The transition temperature from mild to severe wear differs from one to another reinforcement. The ability for the reinforcement to

Table 4 Effect of normal load on the tribological properties of Al and Mg MMCs

References	Matrix	composite	C.C	Result
(Uthayakumar <i>et al.</i> , 2012)	Al	5 wt% SiC and 5 wt% B ₄ C	60 N 4 m/s	– COF decreasing, and gradual increase below C.C. – COF increasing, and rapid increase beyond C.C.
(Natarajan <i>et al.</i> , 2006)	Al	SiC	Block-on-ring, 1–150 N, 0.16 and 0.8 m/s	– Form Al oxide layer which lower COF at lower loads than C.C. – Severe plastic deformation beyond C.C.
(Feng <i>et al.</i> , 2008)	Al 5083	B ₄ C	Pin-on-Disc, 0.6–1.25 m/s, 50–80 N	– Wear rate of the composite with 10 wt% B ₄ C was approximately 40% lower than that of the composite with 5 wt% B ₄ C.
(Hassan <i>et al.</i> , 2015)	Mg	0.7 wt% Y ₂ O ₃ & 0.3 wt% Cu	Pin-on Disc, 5–30 N, 1 m/s up to 1000 m	– Abrasion and delamination are dominant in wear. – At higher load, thermal softening occurs. – Adhesive wear occurs at high test load
(Kumar <i>et al.</i> , 2018)	Mg	0.4 wt% Ce, 1.53 wt% ZnO, 2 wt% and 2.84 wt% Y ₂ O ₃	Scratch Tester, 100–500 mN, 0.15 m/s and 100 m	– Mg with ZnO exhibited more wear resistance than Mg with Y ₂ O ₃ – In Mg/Y ₂ O ₃ , micro cutting wear found to be dominant at lower load and plowing wear at higher load. But in Mg/ZnO combination of micro cutting and micro plowing observed at all loads. – Drop in wear rate with increase in number of scratches
(Manakari <i>et al.</i> , 2019)	Mg	Glass Micro-balloon (GMB)15 wt% and 25 wt%	30 N 3 m/s 600 m	– Higher concentration of GBM foam improve the tribological properties – Formation of oxide layer helps in reducing the wear partially

Abbreviations: Al, aluminum; B₄C, boron carbide; C.C, critical conditions; COF, coefficient of friction; Mg, magnesium; SiC, silicon carbide.

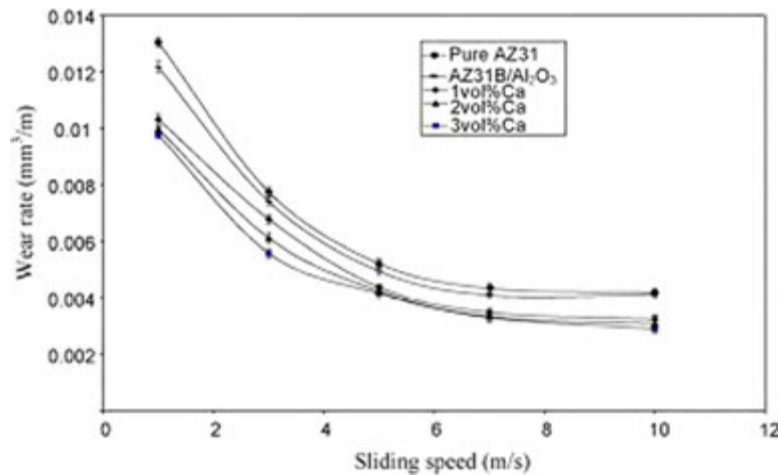


Fig. 8 Effect of sliding speed on wear rate of Al MMCs reinforced with alumina. Reproduced from Shanthy, M., Nguyen, Q.B., Gupta, M., 2010. Sliding wear behavior of calcium containing AZ31B/Al₂O₃ nanocomposites. *Wear* 269 (5-6), 473–479.

withstand higher temperatures before softening was attributed to the layer formation, and dislocations of wear debris. The ability of graphite to sustain higher temperature is due to high friability. However, the addition of graphite reduces strength (Wilson and Alpas, 1996).

These variations in the transition temperatures depend on the type of composites. Critical temperatures have existed, which affect the wear rate and friction coefficient behavior adversely. For instance, using molybdenum disulfide, which exhibits a good self-lubricating property, shows lower wear rate and coefficient of friction. However, once temperature goes beyond 400°C, the solid lubricant oxidizes, and it won't be considered as a good lubricant. Furthermore, the wear rate and friction coefficient of aged aluminum reinforced with SiC under varying temperatures ranging between 20 and 250°C, at a normal load of 20 N, a sliding velocity of 0.5 m/s, and total sliding distance of 2.5 km was studied by Khorshid *et al.* (2013). It was shown that the reinforced matrix exhibited higher wear rate and coefficient of friction than unreinforced aluminum in the temperature range of 25–125°C. However, with a further increase in temperature the wear rate and friction coefficient for the unreinforced aluminum increased sharply, whereas, for the reinforced aluminum it kept decreasing until a temperature of 200°C. After 200°C, even the reinforced aluminum showed a sharp increase in the wear rate and friction coefficient. This was attributed to the softening of the interface between the matrix and the reinforcement particles resulting in the easy pull out of the material (Zhang and Alpas, 1997).

Mg-MMCs reinforced with SiC particles (5, 10, 15 vol%) were evaluated at different temperatures in the range of 25–200°C at a normal load ranging from 5 to 60 N and at a constant sliding velocity of 0.4 m/s. It was observed that at lower temperatures, reinforced and unreinforced composites exhibited a similar behavior in terms of wear rate under normal loads between 5 and 20 N. However, under higher loads, as the volume fraction increased, the reinforced composites showed a lower wear rate as compared to the unreinforced magnesium. The lower wear rate of reinforced composites over pure magnesium was attributed to the higher hardness and strength, which results in more matrix deformation resistance (Labib *et al.*, 2016).

Furthermore, it is shown that as temperature increases, the material load transition decreases. However, as normal load increases, wear transition rate occur from mild to severe wear at each wear temperature. For instant, the transition load decreases from 60 N to 40 N when the temperature changes from 100 to 150°C. When the temperature changes from 150 to 200°C, there was no noticeable change in load transition. The reason for that was attributed to the fact that the temperature going beyond the critical temperature of that composite (Wilson and Alpas, 1996). Below the transition load and temperature, oxidation wear was the main mechanism, while beyond the transition temperature, abrasion and adhesion were predominant. For instant, transition from mild to severe wear occurs at lower loads by increasing temperature from 100 to 150°C. The investigation also showed that as the volume fraction of reinforcements increased, the transition wear decreased (Labib *et al.*, 2016).

Conclusions

It is observed that various factors such as volume fraction of reinforcements, particle size of reinforcement, interface temperature, normal load and sliding speed affect the tribological and mechanical behavior of MMCs. The following specific observations can be drawn from the extensive review presented above.

- (1) The volume fraction of reinforcement has a direct relationship with wear resistance. The particles that are distributed on the surface of the matrix protect the surface from abrasive wear during sliding. However, as the volume fraction increases, wear rate and coefficient of friction decreases under normal conditions; Moreover, under high loads, particles get softened, which results in the increase of wear resistance. The addition of reinforcement is limited to a certain volume fraction of 30 vol%

Table 5 Summary of the effect of operating conditions on the tribological performance of Al and Mg MMCs

Reference	Matrix	Process	Reinforcement	Operating Conditions	Results
(Radhika <i>et al.</i> , 2011)	Al	S.C	Al ₂ O ₃ & Gr	(20,30, and 40) N; (1.5–3.5) m/s; 2100 m	– Wear rate and FC decrease as sliding velocity increase – Composite showing minimum temperature rise than Mg.
(Monikandan <i>et al.</i> , 2016)	AA 6061	S.C	B ₄ C & MoS ₂	20 N; 1000 m	– MoS ₂ formation reduces the wear rate of HMMC up to sliding speed of 2 m/s, then wear rate is going to increase. – Hardness and fracture toughness decreased with increase in MoS ₂
(Liu <i>et al.</i> , 2010)	Al	P.M	AlN	(5–35) N; (0.01–0.08) m/s; 30 min	As sliding velocity increase, Wear rate decreases.
(Lim <i>et al.</i> , 2005)	Mg	DMD	Al ₂ O ₃ (0.22–1.11 vol%)	10 N; (1–10) m/s; 600 m	– Exhibited improved wear resistance – Reinforcement improved the hardness – Abrasion and oxidation are the most predominant wear mechanisms at low speeds, while adhesion at higher speeds.
(Kaviti <i>et al.</i> , 2018)	Mg	P.M	BN (0.5–2.5 wt%)	5–10 N, 0.6–1.2 m/s	0.5 wt% BN reinforced composite showed excellent friction coefficient and wear resistance property as compared to other concentrations.
(Kaviti <i>et al.</i> , 2019)	AZ31	P.M	Al ₂ O ₃ (0.66–1.5 wt%)	5–10 N, 0.6–1.2 m/s and 500–1600 m	– 1.5 wt% Al ₂ O ₃ r reinforced composite showed the highest wear resistance at higher loads – Friction coefficient decrease with increase in load – abrasive and delamination are dominant wear mechanisms

Abbreviations: Al, aluminum; AlN, aluminum nitride; Al₂O₃, aluminum oxide; B₄C, boron carbide; FC, friction coefficient; Gr, graphite; HMMCs, hybrid metal matrix composites; MoS₂, molybdenum disulfide; Mg, magnesium; P.M, powder metallurgy; SiC, silicon carbide; S.C, stir casting.

Table 6 Effect of different reinforcements on the temperature/wear transition of Al MMCs

<i>Composite</i>	<i>Temperature transition (°C)</i>	<i>Types of wear</i>
Al 6061	175–190	Severe
Al A356	225–230	Severe
Al6061/Al ₂ O ₃ 20 vol%	310–350	Severe
Al A356/SiC 20 vol%	440–450	Severe
Al A356/SiC 20 vol%/ Gr 20 vol%	460	Mild

Note: Wilson, S., Alpas, A.T., 1996. Effect of temperature on the sliding wear performance of Al alloys and Al matrix composites. *Wear* 196 (1–2), 270–278.

beyond which the wear rate and friction coefficient become almost independent of the volume fraction. Furthermore, hybrid reinforcement composites exhibit better mechanical and tribological properties.

- (2) Particle size has a predominant effect on the behavior of metal matrix composites. Studies show that in general, as the particle size is reduced, the composites exhibit higher mechanical properties. However, several studies have also showed some unclear results of micron-sized particles. Some studies showed an improved tribological behavior while other showed the opposite. On the other hand, the nano particles have shown improved wear resistance, hardness, and friction coefficient once agglomeration is controlled.
- (3) Normal load is one of the operating conditions that affect the tribological behavior of the composites. As the load increases, both wear rate and friction coefficient are also increased due to the increase in the real area of contact. There is a critical load for each composite in which wear is transferred from mild to severe wear drastically. At lower loads, adhesive wear is predominant, while at higher loads, oxidation wear was found to be a predominant wear mechanism. Once critical load is exceeded, oxide layer breaks resulting in high wear rate.
- (4) Sliding speed is another important parameter that influences the tribological behavior of MMCs. It was observed that it has a linear relationship with wear rate. At lower speeds, the predominant wear mechanism at the interface was found to be abrasion but at higher speeds adhesion and oxidation was found to be a dominant wear mechanism due to thermal softening.
- (5) Elevated temperatures that result mostly due to an increase in the normal load and sliding velocity have a significant effect on the tribological behavior of MMCs. One of the main problems occurring due to the increasing temperature is poor bonding. A better choice of reinforcement may result in improved thermal stability of the composite. However, in general, a composite showed higher thermal stability as compared to the unreinforced metals.

References

- Al-maamari, A.E., Iqbal, A.A., 2019. Wear and mechanical characteristics of Mg-Gr self-lubricating composite fabricated by mechanical alloying. *Journal of Magnesium and Alloys* 7 (2), 283–290.
- Alpas, A.T., Zhang, J., 1992. Effect of particulate reinforcement on the dry sliding wear behavior of aluminum–silicon alloys (A356). *Wear* 155, 83–104.
- Altinkok, N., Ozsert, I., Findik, F., 2013. Dry sliding wear behavior of Al₂O₃/SiC particle reinforced aluminium based MMCs fabricated by stir casting method. *Acta Physica Polonica Series A* 124 (1), 11–19.
- Atthiugan, I., Razal Rose, A., Jebadurai, D.S., 2017. Mechanical and wear behaviour of AZ91D magnesium matrix hybrid composite reinforced with boron carbide and graphite. *Journal of Magnesium and Alloys* 5 (1), 20–25.
- AZoM, 2001. Available at: <https://www.azom.com/properties.aspx?ArticleID=618> (accessed 25.01.21).
- Basavarajappa, S., Chandramohan, G., Mukund, K., Ashwin, M., Prabu, M., 2006. Dry sliding wear behavior of Al 2219/SiCp-Gr hybrid metal matrix composites. *Journal of Materials, Engineering and Performance* 15 (6), 668–674.
- Bodunrin, M., Alaneme, K.K., Chown, L.H., 2015. Aluminum matrix hybrid composites: A review of reinforcement philosophies; mechanical, corrosion and tribological characteristics. *Journal of Materials Research and Technology* 4 (4), 434–445.
- Casati, R., Vedani, M., 2014. Metal matrix composites reinforced by nano-particles – A review. *Metals* 4, 65–83.
- Cerit, A.A., Karamis, M.B., Nair, F., Yildizli, K., 2008. Effect of reinforcement particle size and volume fraction on wear behaviour of metal matrix composites. *Tribology in industry* 30, 31–36. (3&4).
- Choi, H.J., Lee, S.M., Bae, D.H., 2010. Wear characteristic of aluminum-based composites containing multi-walled carbon nanotubes. *Wear* 270, 12–18.
- Dey, A., Pandey, K.M., 2015. Magnesium metal matrix composites –A review. *Reviews on Advanced Materials Science* 42, 58–67.
- Dhanabal, S., Vetrivel, S.D., Rajam, Vimal, 2015. An overview of hybrid metal matrix composites-characterization, directed applications, and future scope. *International Journal of Scientific Engineering and Applied Science* 1 (9), 344–350.
- Donnini, R., 2009. *Metal Matrix Composites*. Version 5.2.2.
- Feng, T., Xiaoling, W., Shirong, G., *et al.*, 2008. Dry sliding friction and wear properties of B4C particulate – Reinforced Al-5083 matrix composites. *Wear* 264, 555–561.
- Gan, Y.X., Daniel, S., Michael, R., 2010. Friction stir processing of particle reinforced composite. *Materials, Materials* 3 (1), 329–350.
- Garces, G., Rodriguez, M., Perez, P., Adeva, P., 2006. Effect of volume fraction and particle size on the microstructure and plastic deformation of Mg–Y₂O₃ composites. *Materials Science and Engineering: A* 419 (1–2), 357–364.
- Moazami-Goudarzi, G., Akhlaghi, F., 2016. Wear behavior of Al 5252 alloy reinforced with micrometric and nanometric SiC particles. *Tribology International* 102, 28–37.
- Gul, F., Acilar, M., 2004. Effect of the reinforcement volume fraction of the dry sliding wear behavior of Al-10Si/Sip composites produced by vacuum infiltration technique. *Composite Science and Technology* 64 (13–14), 1959–1970.
- Hassan, S.F., 2006. Creation of new magnesium-based material using different types of reinforcements. ScholarBank@NUS Repository.

- Hassan, S.F., A., Al-Qutub, M., Tun, K.S., Gupta, M., 2015. Study of wear mechanisms of a novel magnesium based hybrid nanocomposite. *Journal of Tribology* 137 (1), 011601. <https://doi.org/10.1115/1.4028078>.
- Hosseini, N., Karimzadeh, F., Abbasi, M.H., Enayati, M.H., 2010. Tribological properties of Al6061–Al₂O₃ nanocomposite prepared by milling and hot pressing. *Materials & Design* 31 (10), 4777–4785.
- Iruthaya Raj, M.J., Manisekar, K., Gupta, M., 2019. Mechanical and wear properties of Mg/Mo nanocomposites. *Kovove Materialy-Metallic Materials* 57, 237–246.
- Jan, Q., Linan, A., Blau, P.J., 2006. Sliding friction and wear characteristics of Al₂O₃-Al nanocomposites. In: *Proceedings of the STLE/ASME 2006 International Joint Tribology Conference*. doi:10.1115/JTC2006-12326.
- Kaviti, R.V.P., Jeyasimman, D., Parande, G., *et al.*, 2019. Improving the friction and wear characteristics of AZ31 alloy with the addition of Al₂O₃ nanoparticles. *Materials Research Express* 6, 126505.
- Kaviti, R.V.P., Jeyasimman, D., Parande, G., Gupta, M., Narayanasamy, R., 2018. Investigation on dry sliding wear behavior of Mg/BN nanocomposites. *Journal of Magnesium and Alloys* 6, 263–276.
- Khorshid, M.T., Menezes, P.L., Omrani, E., 2013. *Tribology of metal matrix composites*. New York, NY: Springer, pp. 233–268.
- Kumar, A., Keerti, S., Jain, J., *et al.*, 2018. Investigations of wear response of pure Mg and Mg-0.4 Ce-Y₂O₃/ZnO nano composites using a single and repeated scratch tests. *Tribology Transactions* 61 (5), 951–959.
- Labib, F., Ghasemi, H.M., Mahmudi, R., 2016. Dry tribological behavior of Mg/SiCp composites at room and elevated temperature. *Wear* 348–349, 69–79.
- Li, B., Lavernia, E.J., 2015. Spray forming of MMCs. *Comprehensive Composite Materials* 3 (2000), 617–653.
- Lim, C.Y.H., Lim, S.C., Gupta, M., 2003. Wear of magnesium composites with continuous, interconnected wire reinforcement. *Materials Science Forum*. 447–450. (vols. 437–438).
- Lim, C.Y.H., Leo, D.K., Ang, J.J.S., Gupta, M., 2005. Wear of magnesium composites reinforced with nano-sized alumina particulates. *Wear* 259, 620–625.
- Lim, S.C., Gupta, M., Ng, W.B., 1997. Friction and wear characteristics of Al-Cu/C composites synthesized using liquid phase casting process. *Materials and Design* 18 (3), 161–166.
- Liu, Y., Han, Z., Cong, H., 2010. Effects of sliding velocity and normal load on the tribological behavior of a nanocrystalline Al based composite. *Wear* 268 (7–8), 976–983.
- Mamgain, R., Manna, A., Mer, K.K.S., Chauhan, A., 2015. Effect of volume fraction (Al₂O₃ and SiC)p on the Mechanical properties of Al (6061) hybrid metal matrix composite. *International Journal of Scientific & Engineering Research* 6 (5), 189–198.
- Manakari, V., Parande, G., Doddamani, M., Gupta, M., 2019. Evaluation of wear resistance of magnesium/glass microballoon syntactic foams for engineering/biomedical applications. *Ceramics International* 45 (7), 9302–9330.
- Manoj Kumar, B.V., Basu, B., Murthy, V.S.R., Gupta, M., 2005. The role of tribochemistry on fretting wear of Mg-SiC particulate composites. *Composites – Part A* 36, 13–23.
- Moghadam, A.D., Omrani, E., Menezes, P.L., Rohatagi, P.K., 2015. *Mechanical and Tribological Properties of Self-Lubricating Metal Matrix Nanocomposites Reinforced by Carbon Nanotubes (CNTs) and Graphene*. Milwaukee, WI.
- Mondal, A.K., Kumar, S., 2009. Dry sliding wear behavior of magnesium alloy-based hybrid composites in the longitudinal direction. *Wear* 256 (7–8), 705–713.
- Monikandan, V.V., Joseph, M.A., Rajendrakumar, P.K., 2016. Dry sliding wear studies of aluminum matrix hybrid composites. *Resource-Efficient Technologies* 2, S12–S24.
- Narayanasamy, P., Selvakumar, N., 2017. Tensile, compressive and wear behavior of self-lubricating sintered magnesium based composites. *Transaction Nonferrous Material Society of China* 27, 312–323.
- Natarajan, N., Vijayanangan, S., Rajendran, I., 2006. Wear behavior of A356/25SiCp aluminium matrix composites sliding against automobile friction material. *Wear* 261, 812–822.
- Nieto, A., Yang, H., Jiang, L., Schoenung, J.M., 2017. Reinforcement size effects on the abrasive wear of boron carbide reinforced aluminum composites. *Wear* 390–391, 228–235.
- Nturanabo, F., Masu, L., Kirabira, J.B., 2019. Novel Applications of Aluminum MetalMatrix Composites. doi:10.5772/intechopen.86225.
- Panwar, N., Chauhan, A., 2018. Fabrication methods of particulate reinforced Aluminium metal matrix composite – A review. *Materials Today Proceedings* 5 (2), 5933–5939.
- Radhika, N., Subramanian, R., Prasat, S.V., 2011. Tribological behaviour of aluminium/alumina/graphite hybrid metal matrix composite using Taguchi's techniques. *Journal of Minerals and Materials Characterization and Engineering* 10 (5), 427–443.
- Rathaur, A.K., Katiyar, J.K., Patel, V.K., 2019. Experimental analysis of mechanical and structural properties of hybrid aluminium (7075) matrix composite using stir casting method. *IOP Conference Series: Materials Science and Engineering* 653 (1), 012033.
- Sambath, K.M., Navaneethakrishnan, P., 2017. Mechanical and corrosion behavior of Al7075 (Hybrid) metal matrix composites by two step stir casting process. *Latin American Journal of Solids and Structures* 14 (2), 243–255.
- Selvam, B., Marimuthu, P., Narayanasamy, R., *et al.*, 2014. Dry sliding wear behaviour of zinc oxide reinforced magnesium matrix nano-composites. *Materials and Design* 58, 475–481.
- Shanthi, M., Nguyen, Q.B., Gupta, M., 2010. Sliding wear behavior of calcium containing AZ31B/Al₂O₃ nanocomposites. *Wear* 269 (5–6), 473–479.
- Sharma, A.K., Bhandari, R., Aherwar, A., Rimašauskienė, R., Bretotean, C.P., 2020. A study of advancement in application opportunities of aluminum metal matrix composites. *Materials Today Proceedings* 26 (2), 2419–2424.
- Shil, A., Roy, S., Balaji, P.S., *et al.*, 2019. Experimental analysis of mechanical properties of stir casted aluminium-graphene nanocomposites. *IOP Conference Series: Materials Science and Engineering* 653 (1), 012021.
- Shinda, D.M., Sahoo, P., Davim, J.P., 2020. Tribological characterization of particulate-reinforced aluminum metal matrix nanocomposites. *Advanced Composites Letters* 29, 1–29.
- Srinivasan, M., Loganathan, C., Kamaraj, M., *et al.*, 2012. Sliding wear behaviour of AZ31B magnesium alloy and nano-composite. *Transactions of Nonferrous Metals Society of China* 22 (1), 60–65.
- Sujan, D., Oo, Z., Rahman, M.E., Maleque, M.A., Tan, C.K., 2012. Physio-mechanical properties of aluminum metal matrix composites reinforced with Al₂O₃ and SiC. *International Journal of Materials and Metallurgical Engineering* 6 (8), 678–681.
- Uthayakumar, M., Aravindan, S., Rajkumar, K., 2012. Wear performance of Al-SiC-B4C hybrid composites under dry sliding conditions. *Materials & Design* 47, 456–464.
- Weia, T.Z., Shamsuria, S.R., Yeea, C.S., Rashida, M.W.A., Ahsan, Q., 2013. Effect of sliding velocity on wear behavior of magnesium composite reinforced with SiC and MWCNT. *Procedia Engineering* 68, 703–709.
- Wilson, S., Alpas, A.T., 1996. Effect of temperature on the sliding wear performance of Al alloys and Al matrix composites. *Wear* 196 (1–2), 270–278.
- Yashpal, Jawalkar, C.S., Kant, S., *et al.*, 2020. Effect of particle size variation of bagasse ash on mechanical properties of aluminium hybrid metal matrix composites. *Materials Today Proceedings* 21 (4), 2024–2029.
- Zhang, J., Alpas, A.T., 1997. Transition between mild and severe wear in aluminum alloys. *Acta Materialia* 45 (2), 513–528.
- Zhang, M.J., 2008. Effect of graphite particle size on wear property of graphite and aluminum oxide reinforced AZ91D-0.8%Ce composites. *Transactions of Nonferrous Metals Society of China* 18, 237–277.
- Zhang, S., Jiang, F., Ding, W., 2008. Microstructure and mechanical performance of pulsed current gas tungsten arc surface engineered composite coatings on Mg ally reinforced by SiCp particles. *Materials Science And Engineering: A* 490 (1–2), 208–220.

Mechanical and Tribological Properties of Aluminum Based Metal Matrix Nanocomposites

Mir Irfan Ul Haq, Sanjay Mohan, and Ankush Raina, Shri Mata Vaishno Devi University, Katra, Jammu, India
Subramanian Jayalakshmi, Ramachandra Arvind Singh, and Xizhang Chen, Wenzhou University, Wenzhou, China
Sergey Konovalov, Samara National Research University, Samara, Russia
Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Aluminum Based Nanocomposites

The growing environmental concerns in industries and the end users has led to a surge in the use of lightweight materials for various engineering applications (Kumar *et al.*, 2018; Baba *et al.*, 2019). Further, the favorable properties associated with aluminum such as easy castability, better thermal conductivity and ease of machining makes aluminum a good candidate material for a variety of engineering applications particularly for automotive and aerospace applications (Suresh and Moorthi, 2013). Materials used for modern engineering components, particularly in machines, apart from possessing better mechanical properties should exhibit better tribological properties as friction and wear are the main causes of failure in engineering components that undergo relative mechanical motion (Haq and Anand, 2018). Aluminum, in its pure form offers very little structural advantage and also loses its performance capability at elevated temperatures. Apart from poor mechanical properties, aluminum in its pure form, due to its soft nature, also has poor tribological properties. A variety of measures have been adopted previously to address these issues such as: (1) heat treatment of the cast components, (2) alloying aluminum by various agents to form better strength alloys and (3) development of Aluminum Metal Matrix Composites (AMMCs) by reinforcing aluminum by various micro-sized particles (such as SiC, Al₂O₃, TiB₂, Si₃N₄, TiC, B₄C, etc.) (Bodunrin *et al.*, 2015; Omrani *et al.*, 2015). Making of composites provided superior properties than mere heat treatment alone. However, depending on the nature of the reinforcement, composites have some drawbacks, such as poor toughness and ductility, excessive tool wear during machining operation, higher wear rate of counterface materials in tribological systems. It is well known that the reinforcement of aluminum with various ceramic reinforcements leads to increased porosity content, particularly at the matrix-reinforcement interface. Fracture of components is related to porosity content as porosity act as potential sites for crack nucleation. Porosity formation also depends on the reinforcement particle size as it is widely accepted that larger sized particles degrade the inter-particle cohesion. In addition to the aforementioned factors, particle clustering also contributes towards ductility reduction and eventually lowering the fracture toughness. Casting and Powder Metallurgy (PM) are the widely adopted methodologies for development of AMMCs, however due to technical difficulties associated with PM route to produce large sized parts, casting is the more common method. Further, due to the lower melting point of aluminum, casting is more cost-effective route for development of AMMCs.

With the recent developments in the field of nanotechnology, aluminum nanocomposites (NCs) have gained impetus as a material option for various engineering applications, wherein various nano-sized reinforcement (size < 100 nm) are added to aluminum and its alloys. Nanocomposites, if developed through an appropriate processing route can overcome the aforementioned limitations of AMMCs with micron-sized reinforcements. As reported by various researchers, NCs offer higher strength, improved hardness, better ductility, improved fracture toughness and better tribological behavior even at lower reinforcement content as compared to conventional composites (Jayalakshmi and Singh, 2015). Properties of aluminum nanocomposites are enhanced primarily because of smaller size of reinforcements, as large sized particles cause inhomogeneity in matrix. Owing to inhomogeneity, localized stress concentration is experienced near particles, when material is subjected to external loads, thereby causing the material to fail even at lower applied loads (Gnjidić *et al.*, 2001; Lloyd, 1991) and brittleness in the material.

Types of Aluminum Nanocomposites

Aluminum nanocomposites are being proposed for variety of applications because of their better properties in comparison to base matrices. Nanomaterials that are added as reinforcement to aluminum and its alloys in the form of nanoparticles, nanotubes, nano flakes and nanofibers. Fig. 1 shows the classification of different types of nanomaterials used as reinforcement. Graphene based nanocomposites have gained much focus in recent years due to their good strength and elastic modulus. Graphene has high strength of 130 GPa and is the basic building block for CNT's (Carbon nanotubes) and fullerenes (Prashantha Kumar and Xavier, 2014; Jang and Zhamu, 2008).

Studies on use of graphene as a reinforcement have shown better mechanical and tribological properties of the composites. Properties of graphene-based nanocomposites are also dependent upon their volume fraction (or weight fraction). Addition of 0.5–2 vol% of graphene in aluminum composite improved compression strength from 330% to 586% in comparison to that of the base matrix. High tensile strength and good elastic modulus of graphene contributes strongly in enhancing the strength of matrix (Li *et al.*, 2018).

Synthesis of graphene-based nanocomposites remains a challenge due to their poor dispersion and agglomeration (Prashantha Kumar and Xavier, 2017). Better dispersion results in improved ductility of aluminum alloys. Poorly dispersed nanoparticles

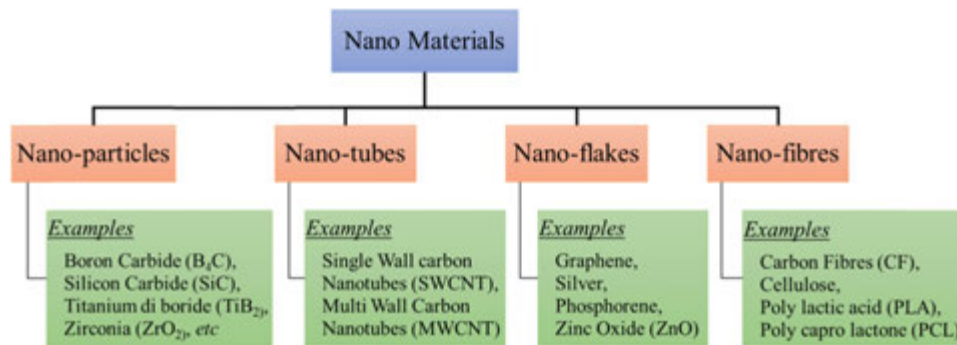


Fig. 1 Classification of nanomaterials used as reinforcement in aluminum nanocomposites.

becomes a cause of agglomeration at interface of grain boundaries, which further leads to development of cracks upon elongation (Boostani *et al.*, 2015a). Boostani *et al.* (2015b) used graphene sheets and SiC as reinforcements in aluminum powder prepared via powder metallurgy route. Their results were compared with SiC in aluminum matrix and graphene encapsulated SiC in aluminum matrix. It was observed that graphene encapsulated SiC resulted in improved yield strength and ultimate tensile strength by 81% and 60%, respectively. This was due to the less agglomeration of SiC particles. Hence, it was observed that graphene encapsulation lead to improvement in dispersion which further improved the mechanical properties.

Some researchers have opined that agglomeration of nanoparticles can be prevented by ball milling aluminum powder with graphene nanoparticles and casting the matrix ultrasonically in semisolid state (Kai *et al.*, 2013; Yang *et al.*, 2004). Results have shown substantial improvements in mechanical properties. However, complete viability of the method can only be established only if other properties such as thermal conductivity and ability of graphene sheets to prevent agglomeration are investigated (Boostani *et al.*, 2015a).

Addition of CNT's and MWCNT's have also resulted in improved strength of nanocomposites. Further, their effect on tribological properties is also substantial, but the issue of uniform distribution of nanotubes needs to be addressed. Wettability issues and lower contact area also affects the properties of nanocomposites having nanotubes (Odom *et al.*, 1998). In the recent past, various studies have been undertaken to address these issues, wherein it was observed that wet ball mixing can be used to improve the dispersion of CNT in aluminum matrix (Laha *et al.*, 2007). Further, ultra-sonication of CNT followed by ball milling with aluminum showed improved dispersion that resulted in refinement of grains (Laha *et al.*, 2007).

Hanizam *et al.* (2019) carried out a study with MCWNT in A-356 aluminum alloy using stir casting process. Their results were obtained for different weight percentage of MCWNT (0.5 wt%, 1 wt%) and magnesium (0.25 wt%, 0.5 wt%) corresponding to varying stirring times. A corresponding improvement of 76.3% and 108.4% in the hardness and UTS was reported for 0.5 wt% MCWNT and 0.5 wt% Mg in comparison to the base matrix. It was also observed that the mechanical properties of aluminum composites containing MCWNT can be enhanced by thixoforming and heat treatment.

Brief Overview of Processing Routes

Nanocomposites, a well-recognized name in the domain of composites has given a good competition to microcomposites. Apart from type of reinforcements, processing routes also influence the properties of NCs. A common distinction amongst various processes for the fabrication of metal matrix nanocomposites can be made based upon the state of the matrix during fabrication. The state can be either molten, semi-solid, or solid. This section briefly presents various processing routes adopted in the development of NCs.

Liquid state processes

Liquid state processes for the development of metal matrix nanocomposites (MMNCs) are the most preferred route due to their cost-effectiveness, simplicity, and potential for producing near-net-shape components (Dehghan Hamedan and Shahmiri, 2012; Mazahery *et al.*, 2009; Sajjadi *et al.*, 2011). Some of the processes related to the liquid state of materials are casting, melt deposition, infiltration, and ultrasonic assisted casting.

Stir casting

Stir casting is the liquid state process which has been widely used for development of MMNCs, due to its economy and simplicity. This method is generally used with a large volume of metal (Clyne and Withers, 1995; Hashim *et al.*, 1999; Surappa, 2003). In this method, mechanical stirring is carried out to mix a dispersed phase in a metal matrix (in the molten form). Efficient mixing is achieved due to the high viscosity of semi-solid matrix material. Stirring carried out in furnace is the critical component of this technique. Molten material produced with reinforced nanoparticles is solidified by die/sand/permanent mold casting. Oxides of magnesium (MgO), aluminum (Al₂O₃), zirconia (ZrO₂) and silicon carbide (SiC) nanoparticles as well as carbon nanotubes (CNTs) have been associated with magnesium and aluminum matrices using stir casting method (Dehghan Hamedan and

Shahmiri, 2012; Hemanth, 2009; Li *et al.*, 2010; Sajjadi *et al.*, 2011; Suresh *et al.*, 2011; Yar *et al.*, 2009). In order to deal with clustering and wetting issues, nanoparticles are ball milled and pre-dispersed on metal powder surface. These powders are then mixed with molten metal through stirring. Nanocomposite synthesis reinforced with CNTs, Al_2O_3 , and SiC have been carried out using this technique (Dehghan Hamedan and Shahmiri, 2012; Karbalaee Akbari *et al.*, 2013b; Mazahery *et al.*, 2009; Mazahery and Shabani, 2012a,b; So *et al.*, 2013; Su *et al.*, 2012a,b).

Ultrasonic assisted casting

This type of casting is considered to be more effective in solving issues of particle clusters that usually result in agglomeration and poor wettability (Cao *et al.*, 2008b; Donthamsetty, 2009). In this method, the melt is treated with ultrasonic waves with a frequency range of 18–20 kHz. This treatment is carried out simultaneously or post to reinforcement phase addition. This technique has been extensively researched for development of Al based nanocomposites by adding reinforcements such as AlN, CNTs, SiC, Al_2O_3 , and B_4C , CNTs, and AlN (Cao *et al.*, 2008a,c; Choi *et al.*, 2012; Donthamsetty, 2009; Lan *et al.*, 2004; Mula *et al.*, 2009; Puga *et al.*, 2013; Yang *et al.*, 2004).

Infiltration process

In this process, a porous preform is injected with pressurized liquid metal. Composites with micro-sized reinforcements have been developed by this technique e.g., SiC particles, AlN, TiC, Al_4C_3 glass fiber, etc. (Balch *et al.*, 1996; Fukunaga and Goda, 1984; Lai and Chung, 1994a,b; Muscat and Drew, 1993; Rohatgi *et al.*, 1998). Preform is prepared from slurry comprising of reinforcement, binder, a liquid carrier. Subsequently, the preform is subjected to drying and heat treatment to retain dimensional stability during the pressure-assisted molten metal infiltration.

Disintegrated melt deposition

This process was employed to carry out homogeneous mixing of nano-reinforcements in aluminum and magnesium alloys. This technique was developed for preparation of discontinuously reinforced MMCs of near-net-shape (Tham *et al.*, 1999) and involves both, casting and spray processes. In this process, ceramic particles are incorporated into molten matrix during stirring of the mix. Composite slurry thus formed is further disintegrated with using inert gas jets at 750°C and is deposited on a metallic substrate. Ingots thus produced are subjected to secondary processes such as extrusion. It is a bottom pouring process and hence (1) eliminates the need for separate melting and pouring units (2) removes oxides and slag/dross with least metal wastage and (3) eliminates retention/settling of nano-reinforcements in crucible (Ceschini *et al.*, 2016).

High pressure die casting

Besides, semi-solid and stir casting methods, high pressure die casting (HPDC) has also been used for the development of MMNCs. As compared to low pressure die casting, this process enables the development of more components with detailed dimensions. In this method, metal in the molten state is forcibly fed into a die cavity. Solidification rate and filling speeds in this process are very high. Due to this, HPDC method is categorized by fast cycle times ranging from few seconds to several minutes, subjected to the size and thickness of the casting. The process also causes entrapment of gas due to high turbulence of metal in die cavity (Long *et al.*, 2012; Wang *et al.*, 2011).

Solid state routes

Synthesis of many nanocomposites has been made by solid-state process of powder metallurgy (PM) technique. Wettability issues between matrix and reinforcement are of no/less concern with this process (Suryanarayana and Al-Aqeeli, 2013). PM process also produces near-net-shape parts. Major advantage of this method is the possibility to form numerous combinations of matrix and reinforcements, and higher volume fraction of reinforcement can be easily incorporated. Automotive industry is using PM process on a large scale for manufacturing of small-sized parts (Cintas *et al.*, 2005). High price of powders and increased porosities are some of the drawbacks of PM process which further require certain secondary processing such as forging, rolling, extrusion, etc., (Ye *et al.*, 2005). Basic steps involved in PM process are (1) mixing of powders, (2) compaction of powders and (3) sintering of powders.

Mixing of powders can be carried out by different methods such as mortar pestle, cone mixing, ball mixing, etc. Compaction of green compacts is carried out by processes such as hot isostatic pressing (HIP), hot extrusion and vacuum hot isostatic pressing (Liu *et al.*, 1994). To consolidate powders, other process such as equal channel angular pressing (ECAP), have been also used (Bera *et al.*, 2013). Similarly, there are different sintering arrangements e.g., conventional sintering in a resistance furnace, induction sintering, microwave sintering, bidirectional hybrid microwave sintering, etc.

Semi-solid state processes

This process is based on partial solid mixtures commonly known as slurries. These mixtures are shaped with solid fractions in the form of small globular grains ranging from 20% to 60%. Commonly, these processes are associated with low porosity, low shrinkage, low processing temperature and non-turbulence. Semi-solid methods can be classified into processes, mainly thixo-processes and rheo-processes.

Thixo-processing

In this process, a solid feedstock is brought into a partly melted state. The base matrix is prepared by partially solidifying liquid melt in controlled atmosphere, and this leads to crystal generation in the slurry. Preparation of feedstock may be done in different ways, e.g., stirring during solidification, ultrasonic treatment and continuous casting by employing magneto-hydrodynamic stirring (Fan, 2002; Dobatkin and Eskin, 1996; Liu *et al.*, 1998). The material in semi-solid state is then injected into dies. Since slurry can be obtained in different ways, this process is considered to be optimized and tailorable for development of MMNCs (Kiuchi and Kopp, 2002).

Rheo-processing

In this process, there is no requirement for a special feedstock. During casting process, the slurry in semi-solid state is prepared from liquid state by cooling process. This process is relatively easy and can be implemented in foundry and the requirement is of standard equipment for handling, treatment, melting, transportation, and degassing. Slurry making is generally the key point in differentiating various approaches. Production of a robust slurry on-demand requires great efforts, and thus different processes evolve. It is worth mentioning here a new technique called New Rheo Casting process (NRC) amongst various rheo-processes techniques. NRC depends on the cooling gradient to create the initial slurry (Yasunori *et al.*, 1996). A large number of crystals are formed when molten metal is poured at low superheat into a holding cup. Thereafter, for the previously set time, the slurry held in the cup, and this leads to growth of crystals. Thereafter, spheroidization of crystals occurs even without additional stirring.

Additive Manufactured Aluminum Nanocomposites

Additive Manufacturing (AM) has evolved as a disruptive technology for development of engineering parts in general, and composites in particular, owing to its (1) ability to handle complex geometries, (2) lower cost even for smaller production volumes, (3) less human interventions, (4) increased product customization and (5) little or no post processing (Chadha *et al.*, 2019). AM technology involves layer-by-layer building up of a part, directly from a CAD geometry, thereby can handle complex geometrical intricacies and results in very less wastage of material (Abdulhameed *et al.*, 2019). Further, limitations encountered in conventional manufacturing such as non-uniform distribution of reinforcing agents, poor wettability of reinforcements inside the molten melt, clustering of reinforcement particles etc. are overcome by the use of AM technology (Gu *et al.*, 2014). A variety of methods of additive manufacturing have been developed having the ability to fabricate parts for a wide range of materials, to print large sized parts having desired mechanical properties with minimum defects. Fig. 2 shows the various AM technologies available for fabricating different materials (Ngo *et al.*, 2018).

With regard to development of aluminum composites, as reported by various researchers, Selective Laser Melting (SLM) and Selective Laser Sintering (SLS) are the commonly used technologies (Ngo *et al.*, 2018). In this direction, Gu and Yuan reported that SLM is not only capable of producing high performance nanocomposites with enhanced properties, but also can generate unique microstructure (Gu and Yuan, 2015). Ma *et al.* (2015) in their work on the development of aluminum based nanocomposites (AlSi10Mg and TiN) prepared by mechanical alloying and SLM have reported that milling prior to SLM plays a key role in evolution of microstructure and uniform distribution of particles in Al-matrix. Further, Vickers' hardness of the developed hybrid composites increased and coefficient of friction (COF) decreased, besides improving the density of composites. In a recent work by Safavi *et al.* (2019), the authors have opined that in comparison to conventional AM technologies, Ultrasonic Additive Manufacturing (UAM) offers advantages because of lower operating temperatures resulting in components with tailored coefficient of thermal expansion (CTE) and less intermetallic compounds. In a related study (Gao *et al.*, 2020) developed TiN/AlSi10Mg nanocomposites by employing ultrasonic vibration technique together with SLM. The authors have reported that TiN nanoparticles play a vital role in grain refinement and 4 wt% TiN nanocomposites exhibited better tensile strength, ductility and microhardness in comparison to conventional composites. The authors attributed this behavior to the improvement in density, grain refinement and resistance offered by uniformly distributed TiN nanoparticles to the dislocation.

In a study by Hu *et al.* (2018), the authors reinforced aluminum by graphene via SLM and reported an 75% improvement in hardness. Similarly, Zhou *et al.* (2019) prepared an aluminum alloy and graphene oxide composite via in-situ method and reported better accuracy. Lin *et al.* (2019) developed aluminum nanocomposites by Laser Additive Manufacturing and reported improvements in yield strength, plasticity and thermal stability as compared to unreinforced aluminum. The improved density, uniformly dispersed nanoparticles, better bonding between Al matrix and nanoparticles and Al matrix, refined grain structure contributes to this behavior.

While AM processed aluminum nanocomposites offer better properties in comparison to conventional manufactured parts, however apart from economic constraints these parts suffer some drawbacks such as:

- (1) Micro-cracking during SLM, due to fast cooling rates (Aboulkhair *et al.*, 2014).
- (2) Porosity due to fast scan speed and formation of oxides (Kaufmann *et al.*, 2016).
- (3) Surface defects and laser spatter (Yang *et al.*, 2019).
- (4) Distortion of shape due to thermal stresses (Buchbinder *et al.*, 2014).

Nevertheless, these limitations can be overcome by selecting the right nanoparticle size and shape and fabricating the parts at optimal process parameters.

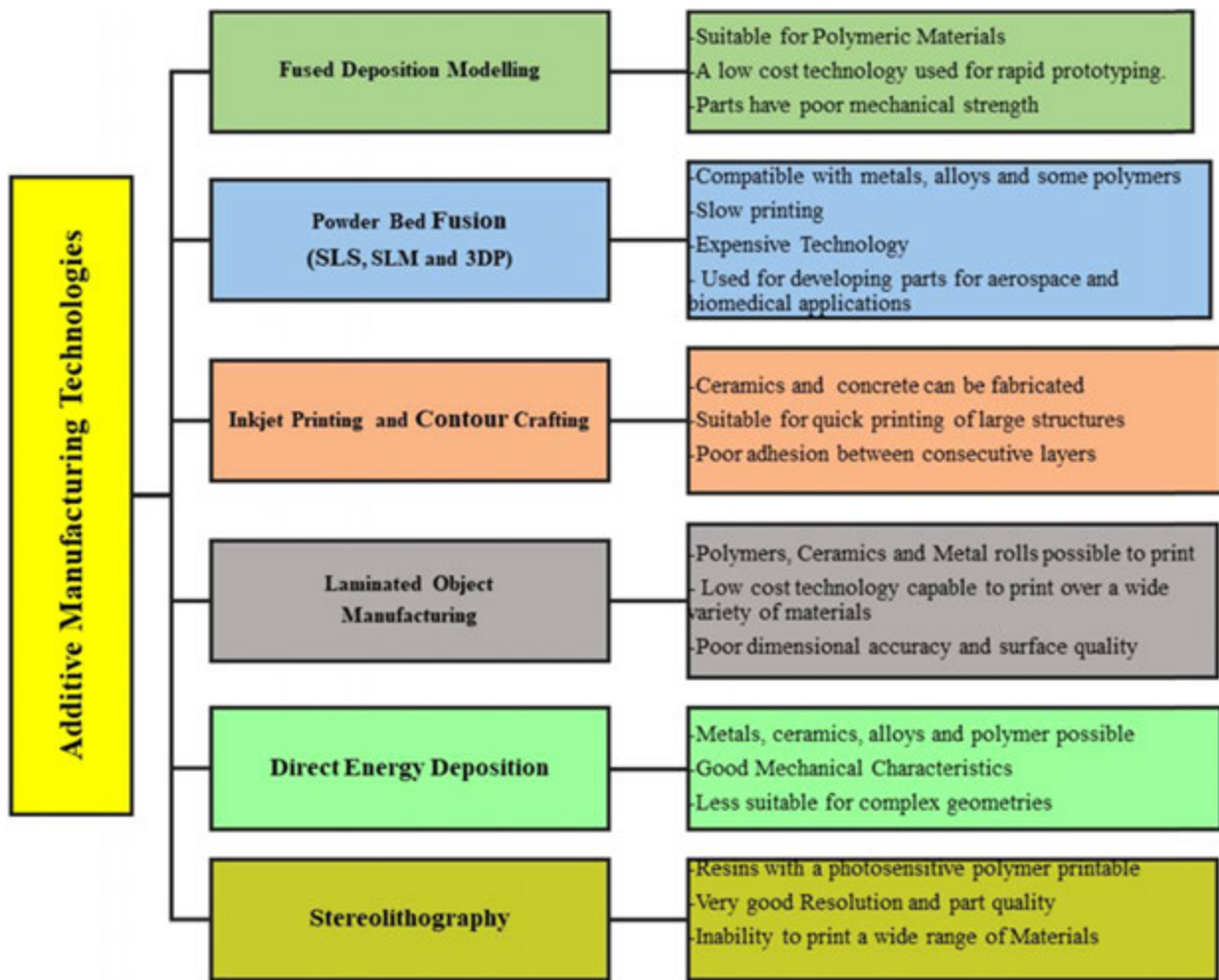


Fig. 2 Different AM Technologies with compatible materials and benefits.

Aluminum Based Nanocomposites: Mechanical Behavior

Composites are developed taking into consideration the desired properties related to specific applications wherein improvement in the mechanical properties in nano reinforced composites than micro reinforced composites. A noteworthy enhancement in yield strength (YS) and ultimate tensile strength (UTS) with the reinforcement of nanoparticles has been reported by researchers (Fig. 3, Ezatpour *et al.*, 2014; Oh *et al.*, 2012; Fig. 4; Sajjadi *et al.*, 2012, 2011; Tahamtan *et al.*, 2013; Yang and Li, 2007). Substantial enhancement in the Young's modulus have also been reported (Karbalaee Akbari *et al.*, 2013a,b; So *et al.*, 2013).

In nanocomposites, improvement in YS values as compared to monolithic aluminum matrix is mainly attributed to grain refinement, improved dislocation density (Sanaty-Zadeh, 2012; Zhang and Chen, 2008). However, improvement in tensile strength is attributed to work hardening mechanism triggered by nanoparticles (Mazahery *et al.*, 2009). Decrease in mechanical properties has been observed by researchers beyond a critical volume/weight reinforcement (Sajjadi *et al.*, 2012; Ezatpour *et al.*, 2014; Mazahery *et al.*, 2009). The decrease is mainly due to the increasing content of nanoparticle clusters and a relatively higher micro-porosity (Ezatpour *et al.*, 2014).

Carbon nanotubes due to their properties have been used as reinforcement by several researchers. Aluminum matrix (Al1060) with carbon nanotubes as reinforcements were developed by friction stir processing (Zhang *et al.*, 2019). Influence of energy input on microstructure and mechanical properties of the composites was investigated. It was observed that the coarsening of grains took place with an increase in energy, and the microstructure revealed uniform incorporation of nanotubes. Higher energy inputs resulted in the 53.8% and 31.2% increase in tensile strength and ductility, respectively as compared to the unreinforced alloy (Fig. 5). Grain refinement, transfer of load, and Orowan looping were the main strengthening mechanisms (Zhang *et al.*, 2019). AlSi10Mg alloys were reinforced with carbon nanotubes (CNTs) using a selective laser melting (SLM) technique (Gu *et al.*, 2019). It was identified that densification behavior of SLM based composites depends upon scan speed and laser power. Their findings have revealed that a fully dense nanocomposite was developed with 350 W laser power and at 2.0 m/s scan speed. These

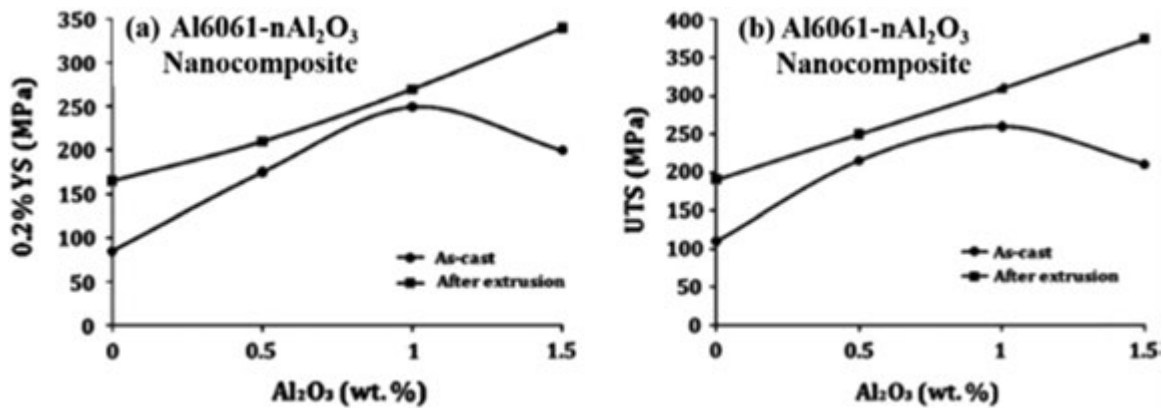


Fig. 3 Enhancement in (a) yield strength (YS) and (b) ultimate tensile strength (UTS) with the Al6061-Al₂O₃ nanocomposite. Reproduced from Ezatpour, H.R., Sajjadi, S.A., Sabzevar, M.H., Huang, Y., 2014. Investigation of microstructure and mechanical properties of Al6061-nanocomposite fabricated by stir casting. *Mater. Des.* 55, 921–928. Available at: <https://doi.org/10.1016/j.matdes.2013.10.060>, Used with permission.

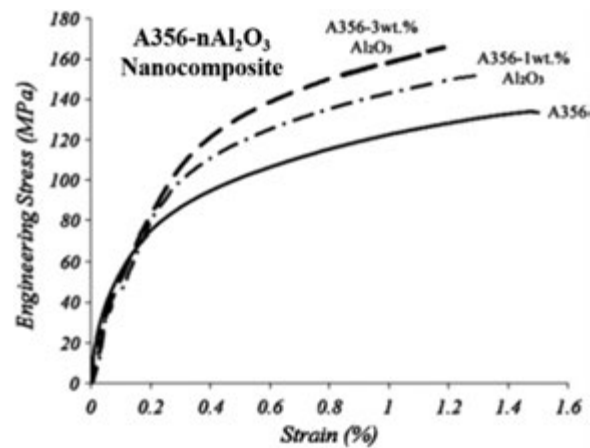


Fig. 4 Tensile stress-strain curves showing enhancement in strength properties of A356 -Al₂O₃ nanocomposite. Reproduced from Sajjadi, S.A., Ezatpour, H.R., Torabi Parizi, M., 2012. Comparison of microstructure and mechanical properties of A356 aluminum alloy/Al₂O₃ composites fabricated by stir and compo-casting processes. *Mater. Des.* 34, 106–111. Available at: <https://doi.org/10.1016/j.matdes.2011.07.037>, Used with permission.

composites have shown increased hardness, tensile strength, and elongation of 154.12 HV, 0.2, 420.8 MPa, and 8.87% (Fig. 6), respectively (Gu *et al.*, 2019). Multi-walled carbon nanotubes (MWCNTs) in weight percentages of 1, 2, and 5 were reinforced in pure Al matrix using powder metallurgy route (Ostovan *et al.*, 2015). The mixture was ball milled followed by compaction and sintering. Ball milling was carried out separately for 0.5, 2, 5, 8, and 12 h. Influence of milling time along with the proportion of MWCNTs on the mechanical properties was reported by the authors. Their findings have revealed that ball milling time influences mechanical properties, and an increase of 60%, 60% and 35% was observed in nano hardness, microhardness and yield strength, respectively (Ostovan *et al.*, 2015). Researchers have attempted to develop carbides at low temperatures, and for this purpose, amorphized graphite was added to the composites (Khorasani *et al.*, 2015). With this technique, wettability issue was resolved. Aluminum was reinforced with amorphous carbon nanotubes (CNTs) using powder metallurgy. The ratio of graphite to CNT used was 1:6. The main objective of this study was to increase the wettability and microhardness of the developed composites. Results showed improvement in wettability and increase in microhardness. This was mainly attributed to the addition of amorphized graphite to CNTs. Improvement in mechanical properties was due to the formation of aluminum carbide (Al₄C₃) which resulted in increased adhesion between CNTs and the aluminum matrix (Khorasani *et al.*, 2015).

Graphene was coated with nano-Al using an organic aluminum reduction method (Zhao *et al.*, 2019). The coated graphene was then mixed with AlSi10Mg alloy by ball milling and nanocomposites were developed using SLM. Mechanical properties and wear behavior of the composites was investigated. Al coating improved the wettability of graphene with Al and resulted in high nucleation rates, thus refining the grains. This increased tensile strength, hardness, and wear resistance (Zhao *et al.*, 2019). Graphene has also been associated as reinforcement in aluminum base matrix using 3D printing. Pure aluminum powder and multi-layered graphene sheets were subjected to ball milling followed by 3D printing using SLM technique (Hu *et al.*, 2018).

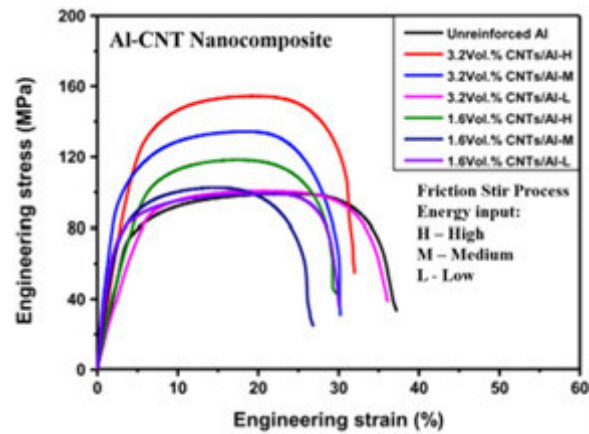


Fig. 5 Engineering stress-strain curves of unreinforced Al and Al-CNT nanocomposite. Reproduced from Zhang, S., Chen, G., Wei, J., *et al.*, 2019. Effects of energy input during friction stir processing on microstructures and mechanical properties of aluminum/carbon nanotubes nanocomposites. *J. Alloy. Compd.* 798, 523–530, Used with permission.

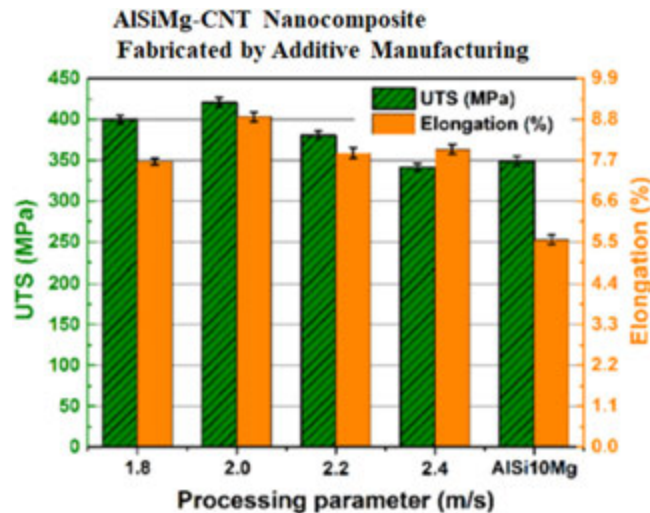


Fig. 6 Ultimate tensile strength (UTS) and elongation of Selective Laser Melting (SLM) fabricated Al-CNT composites with varying scan speed, compared with unreinforced AlSi10Mg specimen fabricated at scan speed of 2.0 m/s. Reproduced from Gu, D., Rao, X., Dai, D., *et al.*, 2019. Laser additive manufacturing of carbon nanotubes (CNTs) reinforced aluminum matrix nanocomposites: Processing optimization, microstructure evolution and mechanical properties. *Addit. Manuf.* 29, 100801, Used with permission.

Graphene was added in three weight percentages of 0.5, 1 and 2.5 respectively. Formation of aluminum carbide (Al_4C_3) observed from XRD analysis, and the results showed an increase of 75.3% in hardness (Vickers) of the fabricated composites as compared to the pure aluminum fabricated through 3D printing (Hu *et al.*, 2018). Graphene platelets have also been reinforced to pure aluminum and the resulting characteristics was compared with other aluminum based composites. Bartolucci *et al.* developed such aluminum-graphene composite using hot isostatic pressing. The main objective of their study was to investigate mechanical properties and compare the same with the CNT reinforced aluminum based composites. The results showed decrease in mechanical properties, which was attributed to the increased formation of aluminum carbide resulting in decreased tensile strength and hardness (Bartolucci *et al.*, 2011). A novel method was used to develop graphene reinforced aluminum matrix (Al-4Cu) nanocomposite containing 0–1 wt% reduced graphene oxide (RGO) (Khoshghadam-Pireyousefan *et al.*, 2020). The fabrication method comprised of high energy ball milling and molecular level mixing. An increase in grain refinement was reported with the increase in the RGO reinforcement. RGO content with graphene has led to the enhancement in the mechanical behavior. Mechanical properties such as ultimate tensile strength, yield strength, and hardness (Vickers) of the developed material were observed to increase by 78%, 49% and 44%, respectively as compared to the base Al-4Cu alloy (Khoshghadam-Pireyousefan *et al.*, 2020).

Nanocomposites containing aluminum as base matrix with B_4C and h-BN as reinforcements were fabricated by stir and ultrasound-assisted casting method (Harichandran and Selvakumar, 2018). One set of samples was prepared with 4 wt% B_4C , and

the other set was prepared with 2 wt% and 4 wt% B_4C , and 2 wt% h-BN. All the developed composites were subjected to mechanical testing. Results showed an improvement by 67% in tensile strength was observed in hybrid nanocomposites as compared to the base matrix. Composites with 6 wt% of B_4C showed maximum hardness and tensile strength. Enhancement in elongation and impact strength was observed in composites with B_4C (2 wt% and 4 wt%) and h-BN (2 wt%) (Harichandran and Selvakumar, 2018). Nanocomposites with nanostructured Al5083 as the base matrix and SiC nanoparticles (SiCnp) as reinforcements in varying proportions were fabricated using mechanical milling route (Tazari and Siadati, 2017). A decrease in grain size was observed with the increase in reinforcement (SiC) content. Increasing the SiCnp content, considerably improved microhardness. An improvement of 95%, 83% and 166% in the compressive strength, shear strengths, and microhardness respectively for the nanocomposite containing 5 wt% SiC (Tazari and Siadati, 2017) was observed. Mousavian *et al.* (2020) reported that changes in the fabrication process lead to an improvement in the properties of nanocomposites. β -SiC nanoparticles were reinforced in aluminum alloy A356. Nickel (Ni) and titanium (Ti) were also used for modifying the surface properties of SiC. The process involved two-way stirring, one in semi solid-state and other in liquid state. Hot rolling process was used to develop the nanocomposites. It was observed that while both Ni and Ti modifiers influenced the mechanical behavior of the developed composites, Ni resulted in maximum enhancement in the properties. An increase by 77%, 85%, and 70% in ultimate tensile strength, yield strength, and strain % was reported in Ni modified composites as compared to the base alloy (Mousavian *et al.*, 2020). A356 was also reinforced with ZrO_2 nanoparticles in 2.5 and 5 wt% using stir casting process (Harsha *et al.*, 2020). Developed composites were investigated for their mechanical properties and the properties were observed to increase with the increase in ZrO_2 weight percentage. An increase by 22.5%, 40%, 39.83%, and 23% were reported in hardness, yield strength, ultimate tensile, and ultimate compressive strength, respectively. However, decrease in elongation was observed, and this was due to the hard and brittle phases of ceramic particles present in the composite (Harsha *et al.*, 2020).

Several authors have reported damage caused to carbon nano-materials while being processed. This had resulted in mechanical energy consumption and unfavorable chemical reactions between matrices and nano-materials (Choi *et al.*, 2011). Due to this very reason, spherical structured fullerenes have also been attempted as reinforcement by researchers owing to their zero-dimensional characteristics. Kwangmin *et al.* (2014) reinforced aluminum with fullerene, in two steps. In the first step, fullerene was crushed into particles of small size and the small-sized fullerenes were mixed with aluminum powder using high energy ball milling. In the next step, composites in the form of sheets were fabricated using hot rolling process. The composites were evaluated for their mechanical behavior and the findings showed hardness of 222 Hv and yield strength of 740 MPa with only 2% volume fraction of fullerenes. Improvement in mechanical properties was attributed to grain refinement and dispersion hardening (Kwangmin *et al.*, 2014).

Aluminum Based Nanocomposites: Tribological Behavior

Tribological performance of aluminum composites is an important area of research. Use of solid lubricants as reinforcement is most suitable for tribological application. Solid lubricants used in aluminum composites include molybdenum di sulfide (MoS_2), tungsten di sulfide (WS_2), graphite, poly tetra fluoro ethylene (PTFE) and graphene.

Singh *et al.* (2018) made Al nanocomposites with WS_2 nanoparticles along with Al_2O_3 and SiC as reinforcements via powder metallurgy technique. They observed that 5 wt% of the nanoparticles resulted in minimum coefficient of friction and wear. Similar kind of investigation was conducted by Ahmadi and Siadati (2018), wherein TiO_2 and CuO nanoparticle additions to aluminum matrix resulted in improvement in mechanical properties. Yield strength increased from 87 MPa to 250 MPa and hardness on Vickers scale increased from 40 to 73 in comparison to the pure aluminum. The authors reported an improvement in anti-wear performance of aluminum with TiO_2 and CuO nanoparticles. Wear coefficient was found to be lower by half in comparison to that of the pure aluminum.

Tribological investigations have also been conducted using graphene nanoparticles in aluminum alloys. (Prashantha Kumar and Xavier, 2017) investigate the tribological performance of aluminum based nanocomposites using graphene as reinforcement. Graphene was added in 0.3, 0.6, 0.9 and 1.2 wt%. They observed substantial decrease in wear for the aluminum composites. Minimum wear was reported for composites containing 0.3 and 0.6 wt% of graphene (Fig. 7). Decrease in COF was reported with the addition of graphene. Minimum COF value observed for the composites for graphene based composites was 0.25 in comparison to the COF of 0.32 for aluminum. Thus, it is inferred that graphene improves tribological characteristics of aluminum. In another study (Prashantha Kumar *et al.*, 2019), the authors used graphene, SWCNT and MWCNT as reinforcements in AA 6061 alloy. They observed that graphene reinforcement resulted in maximum improvement in hardness and fracture toughness due to uniform dispersion and more grain refinement in comparison to the other two reinforcements. Further, due to its protective nature, graphene reinforcement also resulted in minimum wear in comparison to the other two reinforcements. In another study, (Tabandeh-Khorshid *et al.*, 2016) carried out an investigation using graphene in aluminum matrix with 0.1 and 1 wt% of graphene. It was observed that 1 wt% concentration of graphene resulted in minimum coefficient of friction and wear rate (Fig. 8). Results were attributed to the self-lubricating nature of graphene nano particles. From the above discussed literature, it is clear that the use of graphene nanoparticles owing to its intrinsic characterizes leads to the protective film formation between the sliding surfaces. Thus, the use of graphene shall further widen its scope in the field of metal matrix composites.

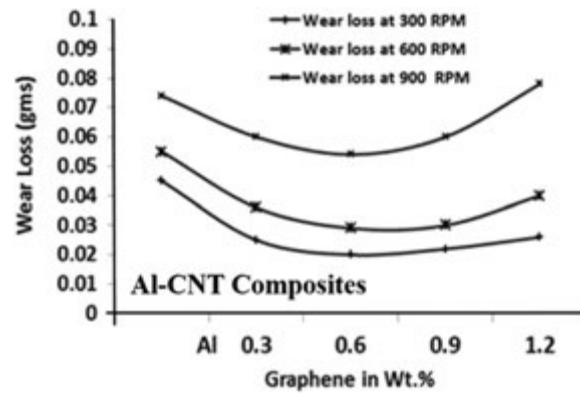


Fig. 7 Substantial decrease in wear for the aluminum-graphene composites as a function of weight percentage of graphene Reproduced from Prashantha Kumar, H.G., Xavier, A.M., 2017. Tribological aspects of graphene-aluminum nanocomposites. In: Kyzas, G. (Ed.), Graphene Materials – Structure, Properties and Modifications 153. IntechOpen.

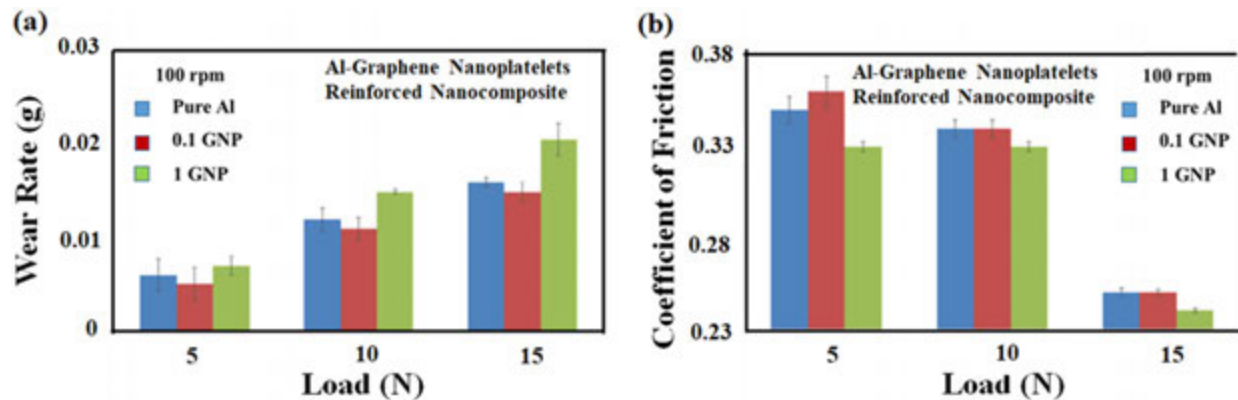


Fig. 8 Variation of (a) wear rate and (b) coefficient of friction, with normal load (N) at sliding speed of 100 rpm for pure Al, Al-0.1 wt% GNP and Al-1 wt% GNP. Reproduced from Tabandeh-Khorshid, M., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2016. Tribological performance of self-lubricating aluminum matrix nanocomposites: Role of graphene nanoplatelets. Eng. Sci. Technol. Int. J. 19, 463–469, Open Access.

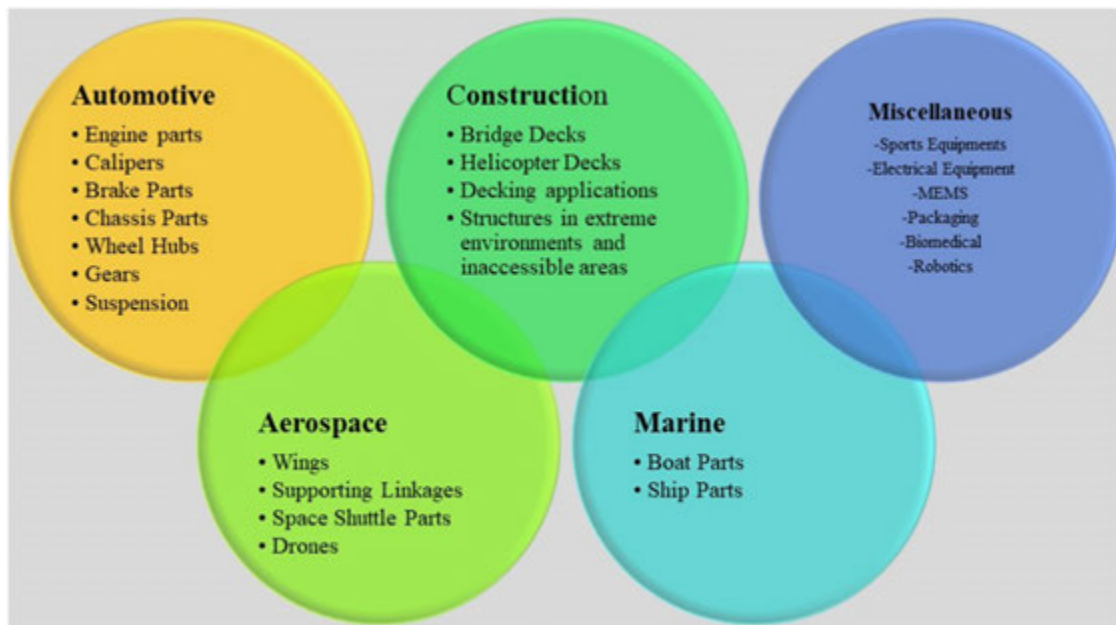


Fig. 9 Potential application areas of aluminum nanocomposites. Reproduced from Nturanabo, F., Masu, L., Kirabira, J.B., 2019. Novel applications of aluminium metal matrix composites. In: Cooke, K. (Ed.), Aluminium Alloys and Composites. IntechOpen. Open Access.

Applications and Challenges

There is increased interest in industries towards the requirement of lightweight materials particularly in automotive and aerospace industries and the dynamic loading environments prevalent in these applications, and in this regard aluminum nanocomposites are promising materials mainly due to their intrinsic properties such as increased strength, high temperature creep resistance (Moghadam *et al.*, 2014). Taking into account the market scenario and the global trends, aluminum nanocomposites could find potential applications in areas such as defense, electrical components, construction, biomedical, sports and recreation industry, nuclear industry, robotic parts, drones, etc. Fig. 9 presents a summary of the potential applications of aluminum nanocomposites. Recent advancements in the development of aluminum nanocomposites by additive manufacturing can further widen the scope of these nanocomposites. Higher thermal conductivity and enhanced strength also makes these nanocomposites suitable for braking applications particularly in aircrafts (Moghadam *et al.*, 2014). Thermal conductivity of these nanocomposites can be varied to suit computer thermal management applications.

Some challenges regarding the development of aluminum nanocomposites that need to be addressed include reinforcement agglomeration, inter-particle interactions and interfacial debonding (Borgonovo and Apelian, 2011). With proper choice of reinforcement content, appropriate synthesis route and optimal process parameters, the aforementioned aspects could be improved, which will further widen the application aluminum nanocomposites.

Conclusions and Future Scope

A summary of the processing routes, mechanical and tribological behavior of aluminum composites has been presented. It has come to the fore that additive manufacturing (AM) has evolved as an alternative and efficient processing route for development of aluminum nanocomposites. Drawbacks associated with aluminum micron-sized reinforced composites can be overcome by using nano-sized reinforcements. Addition of nano-sized reinforcements in aluminum results in improved mechanical and tribological properties even with their addition in small content. Carbon-based nanomaterials such as graphene and CNTs are promising reinforcements for aluminum. The load bearing capacity of the hard nanoparticles and the shearing capability of some of the reinforcements such as graphene, positively influences the mechanical and tribological behavior of these nanocomposites.

Future studies to be undertaken are towards development of cost effective nanocomposites by focussing on developing low cost and efficient synthesis methodologies. A concerted research effort is required towards optimizing the process parameters, augmenting AM with Al nanocomposites, understanding the synergetic behavior of hybrid nano-reinforcements and investigating the properties of these nanocomposites in extreme operating/working environments. Application-oriented research is of prime interest so as to design materials for specific industrial applications particularly for aerospace, automotive, electronics and sports applications.

References

- Abdulhameed, O., Al-Ahmari, A., Ameen, W., Mian, S.H., 2019. Additive manufacturing: Challenges, trends, and applications. *Adv. Mech. Eng.* 11, 1–27. (1687814018822880).
- Aboulkhair, N.T., Everitt, N.M., Ashcroft, I., Tuck, C., 2014. Reducing porosity in AlSi10Mg parts processed by selective laser melting. *Addit. Manuf.* 1, 77–86.
- Ahmadi, M., Siadati, M.H., 2018. Synthesis, mechanical properties and wear behavior of hybrid Al/(TiO₂ + CuO) nanocomposites. *J. Alloy. Compd.* 769, 713–724.
- Baba, Z.U., Shafi, W.K., Haq, M.I.U., Raina, A., 2019. Towards sustainable automobiles-advancements and challenges. *Prog. Ind. Ecol. Int. J.* 13, 315–331.
- Balch, D.K., Mortensen, A., Suresh, S., *et al.*, 1996. Thermal expansion of metals reinforced with ceramic particles and microcellular foams. *Metall. Mater. Trans. A* 27, 3700–3717. <https://doi.org/10.1007/BF02595462>.
- Bartolucci, S.F., Paras, J., Rafiee, M.A., *et al.*, 2011. Graphene–aluminum nanocomposites. *Mater. Sci. Eng. A* 528, 7933–7937.
- Bera, S., Chowdhury, S.G., Estrin, Y., Manna, I., 2013. Mechanical properties of Al7075 alloy with nano-ceramic oxide dispersion synthesized by mechanical milling and consolidated by equal channel angular pressing. *J. Alloy. Compd.* 548, 257–265. <https://doi.org/10.1016/j.jallcom.2012.09.007>.
- Bodunrin, M.O., Alaneme, K.K., Chown, L.H., 2015. Aluminium matrix hybrid composites: A review of reinforcement philosophies; mechanical, corrosion and tribological characteristics. *J. Mater. Res. Technol.* 4, 434–445.
- Boostani, A.F., Tahamtan, S., Jiang, Z.Y., *et al.*, 2015a. Enhanced tensile properties of aluminium matrix composites reinforced with graphene encapsulated SiC nanoparticles. *Compos. Part A Appl. Sci. Manuf.* 68, 155–163.
- Boostani, A.F., Yazdani, S., Mousavian, R.T., *et al.*, 2015b. Strengthening mechanisms of graphene sheets in aluminium matrix nanocomposites. *Mater. Des.* 88, 983–989.
- Borgonovo, C., Apelian, D., 2011. Manufacture of aluminum nanocomposites: A critical review. *Mater. Sci. Forum* 678, 1–22.
- Buchbinder, D., Meiners, W., Pirch, N., Wissenbach, K., Schrage, J., 2014. Investigation on reducing distortion by preheating during manufacture of aluminum components using selective laser melting. *J. Laser Appl.* 26, 012004.
- Cao, G., Konishi, H., Li, X., 2008c. Mechanical properties and microstructure of SiC-reinforced Mg-(2,4)Al-1Si nanocomposites fabricated by ultrasonic cavitation based solidification processing. *Mater. Sci. Eng. A* 486, 357–362. <https://doi.org/10.1016/j.msea.2007.09.054>.
- Cao, G., Koblicka, J., Konishi, H., Li, X., 2008b. Tensile properties and microstructure of SiC nanoparticle-reinforced Mg-4Zn alloy fabricated by ultrasonic cavitation-based solidification processing. *Metall. Mater. Trans. A* 39, 880–886. <https://doi.org/10.1007/s11661-007-9453-6>.
- Cao, G., Choi, H., Oportus, J., Konishi, H., Li, X., 2008a. Study on tensile properties and microstructure of cast AZ91D/AlN nanocomposites. *Mater. Sci. Eng. A* 494, 127–131. <https://doi.org/10.1016/j.msea.2008.04.070>.
- Ceschini, L., Dahle, A., Gupta, M., *et al.*, 2016. *Aluminium and Magnesium Metal Matrix Nanocomposites*. 2016. Singapore: Springer Nature.
- Chadha, A., Haq, M.I.U., Raina, A., *et al.*, 2019. Effect of fused deposition modelling process parameters on mechanical properties of 3D printed parts. *World J. Eng.* 16.
- Choi, H., Konishi, H., Li, X., 2012. Al₂O₃ nanoparticles induced simultaneous refinement and modification of primary and eutectic Si particles in hypereutectic Al–20Si alloy. *Mater. Sci. Eng. A* 541, 159–165.

- Choi, H.J., Shin, J.H., Bae, D., 2011. Grain size effect on the strengthening behavior of aluminum-based composites containing multi-walled carbon nanotubes. *Compos. Sci. Technol.* 71, 1699–1705.
- Cintas, J., Cuevas, F.G., Montes, J.M., Herrera, E.J., 2005. High-strength PM aluminium by milling in ammonia gas and sintering. *Scr. Mater.* 53, 1165–1170. <https://doi.org/10.1016/j.scriptamat.2005.07.019>.
- Clyne, T.W., Withers, P.J., 1995. *An Introduction to Metal Matrix Composites*. Cambridge University Press.
- Dehghan Hamedan, A., Shahmiri, M., 2012. Production of A356-1 wt% SiC nanocomposite by the modified stir casting method. *Mater. Sci. Eng. A* 556, 921–926. <https://doi.org/10.1016/j.msea.2012.07.093>.
- Dobatkin, V., Eskin, G., 1996. Ingots of aluminum alloys with nondendritic structure produced by ultrasonic treatment for deformation in the semi-solid state. In: *Proceedings of the International Conference on Semisolid Processing of Alloys and Composites*, Sheffield, pp. 193–196.
- Donthamsetty, S., 2009. Ultrasonic cavitation assisted fabrication and characterization of A356 metal matrix nanocomposite reinforced with SiC, B₄C, CNTs. *Asian International Journal of Science and Technology in Production and Manufacturing Engineering* 2, 27–34.
- Ezatpour, H.R., Sajjadi, S.A., Sabzevar, M.H., Huang, Y., 2014. Investigation of microstructure and mechanical properties of Al6061-nanocomposite fabricated by stir casting. *Mater. Des.* 55, 921–928. <https://doi.org/10.1016/j.matdes.2013.10.060>.
- Fan, Z., 2002. Semisolid metal processing. *Int. Mater. Rev.* 47, 49–86. <https://doi.org/10.1179/095066001225001076>.
- Fukunaga, H., Goda, K., 1984. Fabrication of fiber reinforced metal by squeeze casting: Pressurized infiltration process of molten aluminum to continuous glass fiber bundle. *Bull. JSME* 27, 1245–1250.
- Gao, C., Wu, W., Shi, J., Xiao, Z., Akbarzadeh, A.H., 2020. Simultaneous enhancement of strength, ductility, and hardness of tin/AlSi10Mg nanocomposites via selective laser melting. *Addit. Manuf.* 34, 101378.
- Gnjidić, Z., Božić, D., Mitkov, M., 2001. The influence of SiC particles on the compressive properties of metal matrix composites. *Mater. Charact.* 47, 129–138.
- Gu, D., Yuan, P., 2015. Thermal evolution behavior and fluid dynamics during laser additive manufacturing of Al-based nanocomposites: Underlying role of reinforcement weight fraction. *J. Appl. Phys.* 118, 233109.
- Gu, D., Wang, H., Chang, F., *et al.*, 2014. Selective laser melting additive manufacturing of TiC/AlSi10Mg bulk-form nanocomposites with tailored microstructures and properties. *Phys. Procedia* 56, 108–116.
- Gu, D., Rao, X., Dai, D., *et al.*, 2019. Laser additive manufacturing of carbon nanotubes (CNTs) reinforced aluminum matrix nanocomposites: Processing optimization, microstructure evolution and mechanical properties. *Addit. Manuf.* 29, 100801.
- Hanizam, H., Salleh, M.S., Omar, M.Z., Sulong, A.B., 2019. Optimisation of mechanical stir casting parameters for fabrication of carbon nanotubes–aluminium alloy composite through Taguchi method. *J. Mater. Res. Technol.* 8, 2223–2231.
- Haq, M.I.U., Anand, A., 2018. Dry sliding friction and wear behavior of AA7075-Si₃N₄ composite. *Silicon* 10, 1819–1829.
- Harichandran, R., Selvakumar, N., 2018. Microstructure and mechanical characterization of (B₄C + h-BN)/Al hybrid nanocomposites processed by ultrasound assisted casting. *Int. J. Mech. Sci.* 144, 814–826.
- Harsha, R.N., Kulkarni, M.V., Babu, B.S., 2020. Study of mechanical properties of aluminium/nano-zirconia metal matrix composites. *Mater. Today: Proc.* 26, 3100–3106.
- Hashim, J., Looney, L., Hashmi, M.S.J., 1999. Metal matrix composites: Production by the stir casting method. *J. Mater. Process. Technol.* 92–93, 1–7. [https://doi.org/10.1016/S0924-0136\(99\)00118-1](https://doi.org/10.1016/S0924-0136(99)00118-1).
- Hemanth, J., 2009. Development and property evaluation of aluminum alloy reinforced with nano-ZrO₂ metal matrix composites (NMMCs). *Mater. Sci. Eng. A* 507, 110–113. <https://doi.org/10.1016/j.msea.2008.11.039>.
- Hu, Z., Chen, F., Xu, J., *et al.*, 2018. 3D printing graphene-aluminum nanocomposites. *J. Alloy. Compd.* 746, 269–276.
- Jang, B.Z., Zhamu, A., 2008. Processing of nanographene platelets (NGPs) and NGP nanocomposites: A review. *J. Mater. Sci.* 43, 5092–5101.
- Jayalakshmi, S., Singh, R.A., 2015. Processing routes, mechanical, and tribological properties of light metal matrix nanocomposites. In: Tyagi, R. (Ed.), *Processing Techniques and Tribological Behavior of Composite Materials*. IGI Global, pp. 1–46.
- Kai, X.Z., Li, Z.Q., Fan, G.L., *et al.*, 2013. Enhanced strength and ductility in particulate-reinforced aluminum matrix composites fabricated by flake powder metallurgy. *Mater. Sci. Eng. A* 587, 46–53.
- Karbalaee Akbari, M., Baharvandi, H.R., Mirzaee, O., 2013a. Fabrication of nano-sized Al₂O₃ reinforced casting aluminum composite focusing on preparation process of reinforcement powders and evaluation of its properties. *Compos. Part B Eng.* 55, 426–432. <https://doi.org/10.1016/j.compositesb.2013.07.008>.
- Karbalaee Akbari, M., Mirzaee, O., Baharvandi, H.R., 2013b. Fabrication and study on mechanical properties and fracture behavior of nanometric Al₂O₃ particle-reinforced A356 composites focusing on the parameters of vortex method. *Mater. Des.* 46, 199–205. <https://doi.org/10.1016/j.matdes.2012.10.008>.
- Kaufmann, N., Imran, M., Wischeropp, T.M., *et al.*, 2016. Influence of process parameters on the quality of aluminium alloy EN AW 7075 using selective laser melting (SLM). *Phys. Procedia* 83, 918–926.
- Khorasani, S., Heshmati-Manesh, S., Abdizadeh, H., 2015. Improvement of mechanical properties in aluminum/CNTs nanocomposites by addition of mechanically activated graphite. *Compos. Part A Appl. Sci. Manuf.* 68, 177–183.
- Khoshtaghadam-Pireyousefan, M., Rahmanifard, R., Orovčík, L., Švec, P., Klemm, V., 2020. Application of a novel method for fabrication of graphene reinforced aluminum matrix nanocomposites: Synthesis, microstructure, and mechanical properties. *Mater. Sci. Eng. A* 772, 138820.
- Kiuchi, M.I., Kopp, R., 2002. Mushy/semi-solid metal forming technology – Present and future. *CIRP Ann.* 51, 653–670.
- Kumar, R., Ul Haq, M.I., Ankush, R.A.A., 2018. Industrial applications of natural fiber reinforced polymer composites – Challenges and opportunities. *J. Sustain. Eng.* 12, 212–220. <https://doi.org/10.1080/19397038.2018.1538267>.
- Kwangmin, C., Jiyeon, S.E.O., Donghyun, B.A.E., Hyunjo, C., 2014. Mechanical properties of aluminum-based nanocomposite reinforced with fullerenes. *Trans. Nonferrous Met. Soc. China* 24, s47–s52.
- Laha, T., Kuchibhatla, S., Seal, S., Li, W., Agarwal, A., 2007. Interfacial phenomena in thermally sprayed multiwalled carbon nanotube reinforced aluminum nanocomposite. *Acta Mater.* 55, 1059–1066.
- Lai, S.W., Chung, D.D.L., 1994a. Phase distribution and associated mechanical property distribution in silicon carbide particle-reinforced aluminium fabricated by liquid metal infiltration. *J. Mater. Sci.* 29, 2998–3016.
- Lai, S.W., Chung, D.D.L., 1994b. Fabrication of particulate aluminium-matrix composites by liquid metal infiltration. *J. Mater. Sci.* 29, 3128–3150. <https://doi.org/10.1007/BF00356655>.
- Lan, J., Yang, Y., Li, X., 2004. Microstructure and microhardness of SiC nanoparticles reinforced magnesium composites fabricated by ultrasonic method. *Mater. Sci. Eng. A* 386, 284–290. <https://doi.org/10.1016/j.msea.2004.07.024>.
- Li, D., Ye, Y., Liao, X., Qin, Q.H., 2018. A novel method for preparing and characterizing graphene nanoplatelets/aluminum nanocomposites. *Nano Res.* 11, 1642–1650.
- Li, Q., Rottmair, C.A., Singer, R.F., 2010. CNT reinforced light metal composites produced by melt stirring and by high pressure die casting. *Compos. Sci. Technol.* 70, 2242–2247. <https://doi.org/10.1016/j.compscitech.2010.05.024>.
- Lin, T.-C., Cao, C., Sokoluk, M., *et al.*, 2019. Aluminum with dispersed nanoparticles by laser additive manufacturing. *Nat. Commun.* 10, 1–9.
- Liu, Y.B., Lim, S.C., Lu, L., Lai, M.O., 1994. Recent development in the fabrication of metal matrix-particulate composites using powder metallurgy techniques. *J. Mater. Sci.* 29, 1999–2007. <https://doi.org/10.1007/BF01154673>.
- Liu, C., Pan, Y., Aoyama, S., 1998. In: Bashin, A., More, J., Young, K., Midson, S. (Eds.), *Proceedings of the 5th International Conference on Semisolid Processing of Alloys and Composites*. pp. 439–447.
- Lloyd, D.J., 1991. Aspects of fracture in particulate reinforced metal matrix composites. *Acta Metall. Mater.* 39, 59–71.

- Long, A., Thornhill, D., Armstrong, C., Watson, D., 2012. Predicting die life from die temperature for high pressure dies casting aluminium alloy. *Appl. Therm. Eng.* 44, 100–107. <https://doi.org/10.1016/j.applthermaleng.2012.03.045>.
- Ma, C., Gu, D., Dai, D., *et al.*, 2015. Aluminum-based nanocomposites with hybrid reinforcements prepared by mechanical alloying and selective laser melting consolidation. *J. Mater. Res.* 30, 2816–2828. doi:10.1557/jmr.2015.267.
- Mazahery, A., Shabani, M.O., 2012a. Characterization of cast A356 alloy reinforced with nano SiC composites. *Trans. Nonferrous Met. Soc. China* 22, 275–280. [https://doi.org/10.1016/S1003-6326\(11\)61171-0](https://doi.org/10.1016/S1003-6326(11)61171-0).
- Mazahery, A., Shabani, M.O., 2012b. Nano-sized silicon carbide reinforced commercial casting aluminum alloy matrix: Experimental and novel modeling evaluation. *Powder Technol.* 217, 558–565. <https://doi.org/10.1016/j.powtec.2011.11.020>.
- Mazahery, A., Abdizadeh, H., Baharvandi, H.R., 2009. Development of high-performance A356/nano- Al_2O_3 composites. *Mater. Sci. Eng. A* 518, 61–64. <https://doi.org/10.1016/j.msea.2009.04.014>.
- Moghadam, A.D., Schultz, B.F., Ferguson, J.B., *et al.*, 2014. Functional metal matrix composites: Self-lubricating, self-healing, and nanocomposites – An outlook. *JOM* 66, 872–881.
- Mousavian, R.T., Behnamfar, S., Khosroshahi, R.A., *et al.*, 2020. Strength-ductility trade-off via SiC nanoparticle dispersion in A356 aluminium matrix. *Mater. Sci. Eng. A* 771, 138639.
- Mula, S., Padhi, P., Panigrahi, S.C., Pabi, S.K., Ghosh, S., 2009. On structure and mechanical properties of ultrasonically cast Al–2% Al_2O_3 nanocomposite. *Mater. Res. Bull.* 44, 1154–1160. <https://doi.org/10.1016/j.materresbull.2008.09.040>.
- Muscat, D., Drew, R.A.L., 1993. A method of measuring metal infiltration rates in porous preforms at high temperature. *J. Mater. Sci. Lett.* 12, 1567–1569.
- Ngo, T.D., Kashani, A., Imbalzano, G., Nguyen, K.T.Q., Hui, D., 2018. Additive manufacturing (3D printing): A review of materials, methods, applications and challenges. *Compos. Part B Eng.* 143, 172–196.
- Odom, T.W., Huang, J.-L., Kim, P., Lieber, C.M., 1998. Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature* 391, 62–64.
- Oh, S.-I., Lim, J.-Y., Kim, Y.-C., *et al.*, 2012. Fabrication of carbon nanofiber reinforced aluminum alloy nanocomposites by a liquid process. *J. Alloy. Compd.* 542, 111–117. <https://doi.org/10.1016/j.jallcom.2012.07.029>.
- Omrani, E., Moghadam, A.D., Menezes, P.L., Rohatgi, P.K., 2015. Influences of graphite reinforcement on the tribological properties of self-lubricating aluminum matrix composites for green tribology, sustainability, and energy efficiency – A review. *Int. J. Adv. Manuf. Technol.* 83, 325–346. <https://doi.org/10.1007/s00170-015-7528-x>.
- Ostovan, F., Matori, K.A., Toozandehjani, M., *et al.*, 2015. Effects of CNTs content and milling time on mechanical behavior of MWCNT-reinforced aluminum nanocomposites. *Mater. Chem. Phys.* 166, 160–166.
- Prashantha Kumar, H.G., Xavier, M.A., 2014. Graphene reinforced metal matrix composite (GRMMC): A review. *Procedia Eng.* 97, 1033–1040.
- Prashantha Kumar, H.G., Xavier, M.A., 2017. Tribological aspects of graphene-aluminum nanocomposites. In: Kyzas, G. (Ed.), *Graphene Materials – Structure, Properties and Modifications* 153. IntechOpen.
- Prashantha Kumar, H.G., Joel, J., Xavier, M.A., 2019. Effect of reinforcement surface area on tribological behaviour of aluminium alloy nanocomposites. *Procedia Manuf.* 30, 224–230.
- Puga, H., Barbosa, J., Costa, S., *et al.*, 2013. Influence of indirect ultrasonic vibration on the microstructure and mechanical behavior of Al–Si–Cu alloy. *Mater. Sci. Eng. A* 560, 589–595. <https://doi.org/10.1016/j.msea.2012.09.106>.
- Rohatgi, P., Guo, R., Iksan, H., Borchelt, E., Asthana, R., 1998. Pressure infiltration technique for synthesis of aluminum–fly ash particulate composite. *Mater. Sci. Eng. A* 244, 22–30. [https://doi.org/10.1016/S0921-5093\(97\)00822-8](https://doi.org/10.1016/S0921-5093(97)00822-8).
- Safavi, M.S., Azamiya, A., Farshbaf Ahmadipour, M., Reddy, M.V., 2019. New-emerging approach for fabrication of near net shape aluminum matrix composites/nanocomposites: Ultrasonic additive manufacturing. *J. Ultrasonic Grained Nanostruct. Mater.* 52, 188–196.
- Sajjadi, S.A., Ezalpour, H.R., Beygi, H., 2011. Microstructure and mechanical properties of Al– Al_2O_3 micro and nano composites fabricated by stir casting. *Mater. Sci. Eng. A* 528, 8765–8771. <https://doi.org/10.1016/j.msea.2011.08.052>.
- Sajjadi, S.A., Ezalpour, H.R., Torabi Parizi, M., 2012. Comparison of microstructure and mechanical properties of A356 aluminum alloy/ Al_2O_3 composites fabricated by stir and compo-casting processes. *Mater. Des.* 34, 106–111. <https://doi.org/10.1016/j.matdes.2011.07.037>.
- Sanaty-Zadeh, A., 2012. Comparison between current models for the strength of particulate-reinforced metal matrix nanocomposites with emphasis on consideration of Hall–Petch effect. *Mater. Sci. Eng. A* 531, 112–118. <https://doi.org/10.1016/j.msea.2011.10.043>.
- Singh, N., Mir, I.U.H., Raina, A., *et al.*, 2018. Synthesis and tribological investigation of Al–SiC based nano hybrid composite. *Alex. Eng. J.* 57, 1323–1330.
- So, K.P., Jeong, J.C., Park, J.G., *et al.*, 2013. SiC formation on carbon nanotube surface for improving wettability with aluminum. *Compos. Sci. Technol.* 74, 6–13. <https://doi.org/10.1016/j.compscitech.2012.09.014>.
- Su, H., Gao, W., Zhang, H., *et al.*, 2012b. Study on preparation of large sized nanoparticle reinforced aluminium matrix composite by solid-liquid mixed casting process. *Mater. Sci. Technol.* 28, 178–183. <https://doi.org/10.1179/1743284711Y.0000000009>.
- Su, Hai, Gao, W., Feng, Z., Lu, Z., 2012a. Processing, microstructure and tensile properties of nano-sized Al_2O_3 particle reinforced aluminum matrix composites. *Mater. Des.* 36, 590–596. <https://doi.org/10.1016/j.matdes.2011.11.064>.
- Surappa, M.K., 2003. Aluminium matrix composites: Challenges and opportunities. *Sadhana* 28, 319–334.
- Suresh, S., Moorthi, N.S.V., 2013. Process development in stir casting and investigation on microstructures and wear behavior of TiB_2 on A16061 MMC. *Procedia Eng.* 64, 1183–1190. <https://doi.org/10.1016/j.proeng.2013.09.197>.
- Suresh, S.M., Mishra, D., Srinivasan, A., Arunachalam, R.M., Sasikumar, R., 2011. Production and characterization of micro and nano Al_2O_3 particle-reinforced LM25 aluminium alloy composites. *ARPN J. Eng. Appl. Sci.* 6, 94–98.
- Suryanarayana, C., Al-Aqeeli, N., 2013. Mechanically alloyed nanocomposites. *Prog. Mater. Sci.* 58, 383–502. <https://doi.org/10.1016/j.pmatsci.2012.10.001>.
- Tabandeh-Khorshid, M., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2016. Tribological performance of self-lubricating aluminum matrix nanocomposites: Role of graphene nanoplatelets. *Eng. Sci. Technol. Int. J.* 19, 463–469.
- Tahamtan, S., Halvae, A., Emamy, M., Zabihi, M.S., 2013. Fabrication of Al/A206– Al_2O_3 nano/micro composite by combining ball milling and stir casting technology. *Mater. Des.* 49, 347–359. <https://doi.org/10.1016/j.matdes.2013.01.032>.
- Tazari, H., Siadati, M.H., 2017. Synthesis and mechanical properties of aluminum alloy 5083/SiCnp nanocomposites. *J. Alloy. Compd.* 729, 960–969.
- Tham, L., Gupta, M., Cheng, L., 1999. Influence of processing parameters on the near-net shape synthesis of aluminium-based metal matrix composites. *J. Mater. Process. Technol.* 89–90, 128–134. [https://doi.org/10.1016/S0924-0136\(99\)00002-3](https://doi.org/10.1016/S0924-0136(99)00002-3).
- Wang, L., Turnley, P., Savage, G., 2011. Gas content in high pressure die castings. *J. Mater. Process. Technol.* 211, 1510–1515. <https://doi.org/10.1016/j.jmatprotec.2011.03.024>.
- Yang, T., Liu, T., Liao, W., *et al.*, 2019. The influence of process parameters on vertical surface roughness of the AlSi10Mg parts fabricated by selective laser melting. *J. Mater. Process. Technol.* 266, 26–36.
- Yang, Y., Li, X., 2007. Ultrasonic cavitation based nanomanufacturing of bulk aluminum matrix nanocomposites. *J. Manuf. Sci. Eng.* 129, 497–501. <https://doi.org/10.1115/1.2714583>.
- Yang, Y., Lan, J., Li, X., 2004. Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Mater. Sci. Eng. A* 380, 378–383. <https://doi.org/10.1016/j.msea.2004.03.073>.
- Yar, A., Montazerian, M., Abdizadeh, H., Baharvandi, H.R., 2009. Microstructure and mechanical properties of aluminum alloy matrix composite reinforced with nano-particle MgO. *J. Alloy. Compd.* 484, 400–404. <https://doi.org/10.1016/j.jallcom.2009.04.117>.
- Yasunori, M., Hiroto, T., Atsushi, S., 1996. Method and apparatus for shaping semisolid metals. EP0745694B1.

- Ye, J., He, J., Schoenung, J.M., 2005. Cryomilling for the fabrication of a particulate B 4C reinforced Al nanocomposite: Part I. Effects of process conditions on structure. *Metall. Mater. Trans. A* 37, 3099–3109.
- Zhang, S., Chen, G., Wei, J., *et al.*, 2019. Effects of energy input during friction stir processing on microstructures and mechanical properties of aluminum/carbon nanotubes nanocomposites. *J. Alloy. Compd.* 798, 523–530.
- Zhang, Z., Chen, D.L., 2008. Contribution of Orowan strengthening effect in particulate-reinforced metal matrix nanocomposites. *Mater. Sci. Eng. A* 483–484, 148–152. <https://doi.org/10.1016/j.msea.2006.10.184>.
- Zhao, Z., Bai, P., Misra, R.D.K., *et al.*, 2019. AlSi10Mg alloy nanocomposites reinforced with aluminum-coated graphene: selective laser melting, interfacial microstructure and property analysis. *J. Alloy. Compd.* 792, 203–214.
- Zhou, W., Dong, M., Zhou, Z., *et al.*, 2019. In situ formation of uniformly dispersed Al_4C_3 nanorods during additive manufacturing of graphene oxide/Al mixed powders. *Carbon* 141, 67–75.

Further Reading

- Kaufmann, H., Uggowitzer, P.J., 2001. Fundamentals of the new rheocasting process for magnesium alloys. *Adv. Eng. Mater.* 3, 531–539.

Damping Characteristics of Metal Matrix Composites

Penchal Reddy Matli and Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

The mechanical, thermal, and tribological properties have emerged the metal matrix composites (MMCs) as a prominent structural material (Davis and Artz, 1995; Ibrahim *et al.*, 1991; Miracle, 2005). They also have an impact in automotive, submersible vehicles, and aerospace structure applications (Gupta *et al.*, 2012; Rawal, 2001; Zweben, 1992) that undergo dynamic loading conditions and temperature variations throughout their service life. There is a huge advantage in the pre-existed applications mainly in automotive, aerospace structures, and heavy machineries with high mechanical vibration and damping capability of material (Sastry *et al.*, 2001; Zhang *et al.*, 1993) which is a positive motive towards the tailored MMCs. The combined characteristics such as mechanical vibrations and damping properties will help in opting the material and attains a huge performance.

Lightweight composite materials remain higher damping capabilities (Shunmugasamy *et al.*, 2016) are of great interests to material designers satisfying ever changing demands in automotive, aerospace and marine sectors. The ability of a material to absorb and disappear the mechanical vibrations at the period of cyclic loading is called its damping capacity (Kumar *et al.*, 2017), which were not required to engineering applications as they affect structural stability and then material's efficiency. In general, many of the metals and alloys possess lower damping capacity (Li *et al.*, 2000) so they were limited in their applications and as well as the performance in dynamic structures. All the above observations conclude that there is huge demand for the materials with high damping capacity as they were capable of eliminating unwanted noise and vibration, enhancing vehicle and instrument stability.

In the context of highly advanced technology and modernization, the noise and vibration have become a notable prominent and hazardous impact mainly in the complex mechanical engineering systems. (Yang *et al.*, 2017). Additionally, the vibrations and the sound were efficiently eliminated by the application of Mg or Al based composites as a damping material. In spite of inconsistency, when compared to viscoelastic polymers the damping characteristics of Mg or Al based composites were much dominant than the dense materials (Gupta and Wong, 2015; Wu *et al.*, 2006). The conventional particles reinforced metal matrix composites (MMCs) with high strength and stiffness were refined with enhanced damping properties in the recognized line. While considering the advanced systems in mechanical engineering, the vibrations and sound have been not favorable and became one of the prominent ranges of threat with the vast evolution in the science and technology. This grabbed the damping materials a huge attention. The high specific stiffness, excellent energy/sound absorption properties, low density have marked light weight Mg, Al and their respective alloys as an assured engineering materials.

Metal matrix composites are the potential materials systems designed by the addition of BN, SiC, CeO₂, Sm₂O₃, B₄C, SiO₂, NiTi and metastable reinforcements into Mg or Al matrix to discriminate improvements in both, strength and damping capabilities (Kujur *et al.*, 2017, 2018; Matli *et al.*, 2020; Narasimalu and Gupta, 2006; Nguyen *et al.*, 2015; Parande *et al.*, 2016; Penchal Reddy *et al.*, 2018; Tekumalla *et al.*, 2019). Moreover, addition of such hard, high damping reinforcements in the matrix can modify the microstructure of metals and alloys altering energy dissipation sources. The varying volume fractions, size of the reinforcement and selecting high damping reinforcing materials will influence the damping capacity of the obtained MMC (Siva *et al.*, 2015). The potential of the MMCs have been an efficient class of modern engineering materials, which have been concluded from different structural applications.

The enhancement in the mutual relations in between density and MMCs damping properties will provide a way for evolution of improved materials and which helps in reducing weights in considerable range. Lesser damping capacity was exhibited by traditional structural materials such as steel and titanium (Lu *et al.*, 2009; Prasad *et al.*, 2015). So, the demand for materials with low density and high damping capacity have been raised gradually that can fulfill the above-mentioned applications. Efforts are being pursued thoroughly in developing lightweight high performance composite materials that are tailored to exhibit good mechanical properties and high damping properties (Rahiman and Smart, 2019; Shunmugasamy *et al.*, 2016). Owing to their lower densities, low cost, processing flexibility, heat treat treatment capability, reasonably high thermal conductivity, and low melting point aluminum ($\rho = 2.7$ g/cc) and magnesium ($\rho = 1.74$ g/cc) are most sought-after materials in design of several dynamic structures in semiconductor equipment, aerospace and defense sectors (Gupta and Wong, 2015).

Material selection in dynamic loadings is primarily based on specific stiffness (E/ρ), replacing magnesium with aluminum results in lower values of mass and inertia as both metals have similar specific stiffness. Further, the damping capacity of pure magnesium was found to be 10 and 100 times higher than the pure Al (Schaller, 2003) and 316 stainless steel (Nguyen *et al.*, 2015), respectively. These exceptionally higher damping values of light metals helps in dissipating energy effectively in automotive and electronic components, minimizing fretting damages (Anilchandra and Surappa, 2012). In spite of its high damping capacity magnesium has a dominant priority among all other lightweight materials. With the addition of hard reinforcing particles to the ductile metallic matrix i.e., Mg or Al assists to enhance stiffness and overall damping capacity. This helps in reducing the vibrational amplitude of the mechanical system effectively (Srikanth *et al.*, 2003; Srikanth and Gupta, 2001).

The overall damping enhancement of magnesium or aluminum alloys and its composites can be attributed to several mechanisms like microstructural defects, grain boundary damping, porosity, intrinsic damping capability of the particles, interface damping, thermoelastic damping, thermal mismatch between the particulate and the matrix (Lu *et al.*, 2009; Surappa, 2003).

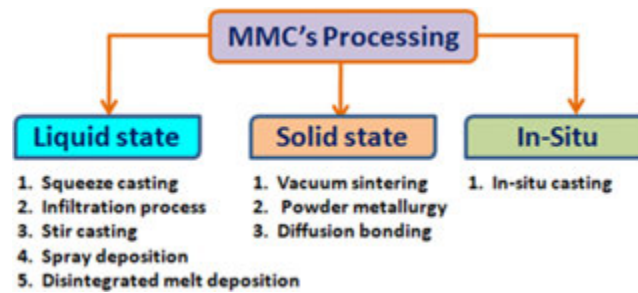


Fig. 1 Various categories of processing of metal matrix composites.

The main aim of the present study is to concentrate on lightweight structural metals such as Al and Mg. This can conclude that the composites with high damping parameters were about to be established and the scope for future research have been determined.

Processing Routes for Metal Matrix Composites

Metal matrix composites (MMCs) have many advantages as compared to monolithic metals as discussed above so their applications are increasing day by day in various fields.

In order to optimize the microstructure and damping properties of metal matrix composites, a variety of processing methods have been developed by industry and researchers over the last two decades. Generally, MMC fabrication can be classified into three categories: (1) Liquid-State processing, (2) Solid-State processing, and (3) In-Situ processing. [Fig. 1](#) shows the various categories of processing of metal matrix composites.

Liquid State Processing

Squeeze casting

Molten metal is introduced into an open die. The dies are then closed so that the molten metal solidifies under pressure within the dies. The heat is rapidly transferred from the molten metal to the dies under high pressure and through the contact between the metal and the die surface. As a result, a fine-grain casting with little to no pore is produced using this method ([Surappa, 2003](#)).

Infiltration process

Liquid metal alloy is infiltrated into the porous forms of fibers/whiskers reinforcements. The volume fraction of the reinforcements usually ranges from 10% to 70%, depending on the level of porosity. Silica and metal-based mixtures are often employed as binder to retain the integrity and shape of the porous forms ([S-de-la-Muela et al., 2020](#)). The phenomenon of transferring of molten metal into a preform is defined as infiltration. In pressure infiltration or melt infiltration, the reinforcements are kept in the die primarily and then the molten alloy is drilled upon the reinforcements and allowed to solidify in the absence of external pressure.

Stir casting

Particulate reinforcements are mixed with liquid metal melt and the mixture then solidifies. Specifically, the pre-treated particles are inserted into the vortex of molten alloy, which is created by a rotating impeller. A problem arises during the stir casting process as the reinforcements are not uniformly distributed and form sediments in the molten alloy. Generally, up to 30% particles in the size of 5–100 μm can be incorporated into the metal alloy ([Ramanathan et al., 2019](#)). [Zhang et al. \(2006\)](#) developed magnesium composites via stir casting method. They have concluded that the damping capacity of 8 wt%TiC/AZ91 was higher than that of AZ91 alloy due to the addition of TiC particulates.

Spray deposition

Spray decomposition can be defined as the phenomenon of atomizing matrix material by which fine diffusion of droplets through the pressure controlled inert gas jets which were filled with heated reinforcement particles. They reported that the deposition of reinforcing elements to the matrix have modified the technique. The minimum reaction of reinforcement with matrix can be attained by higher production rate and solidification time ([Ramanathan et al., 2019](#)). The size and percentage of reinforcement determines the particles the particles distribution in the composite. [Zhang et al. \(1994\)](#) studied the effect of SiC and graphite particulates on the damping behavior of metal matrix composites by spray atomization and deposition technique. They have reported that the damping mechanism related to Al/SiC composites have assigned to dislocation damping, interface damping at low testing temperatures and grain boundary damping, interface damping at high testing temperatures. When compared to Al/SiC, the Al/Gr composites possessed low elastic modulus.

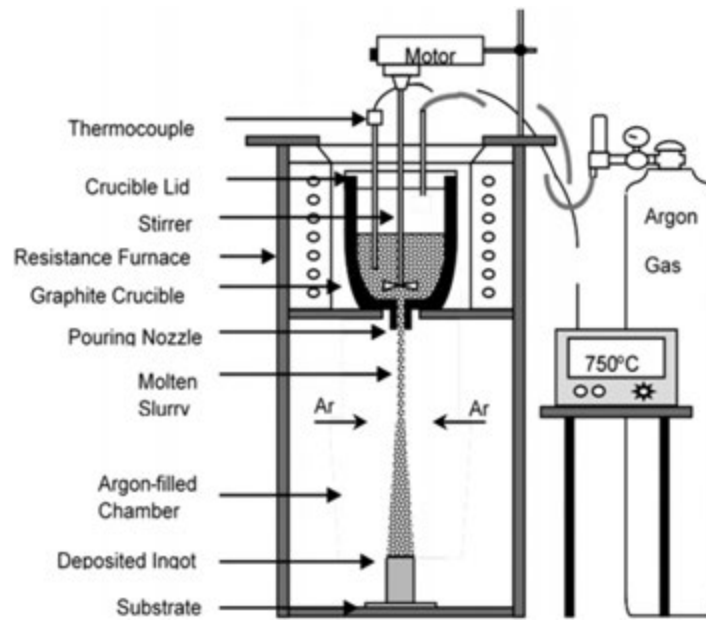


Fig. 2 Schematic diagram for DMD method.

Disintegrated melt deposition (DMD)

Gupta and Wong (2015) examined the novel “Disintegrated Melt Deposition (DMD)” that addresses the consequences that occurs with conventional casting.

The DMD technique helps in uniform distribution of reinforcement, the interfacial integrity among the reinforcement and the matrix which has strong influence on the mechanical properties. This DMD evolved from the spray atomization and deposition technique which developed earlier. This process was shown in Fig. 2.

In this process, through the central drilled hole in the graphite crucible, the composite melt was poured which was fabricated by mechanical stir casting. At a perpendicular to melt stream two linear argon gas jets disintegrates the stream of the melt. On the metallic substrate placed at a certain distance from the gas integration, the composite melt slurry was deposited subsequently. Nguyen *et al.* (2015) investigated the effect of adding metastable particles on the mechanical damping behavior of extruded Mg-Al₈₅Ti₁₅ composites using DMD. The addition of Al₈₅Ti₁₅ powder significantly enhanced the damping properties of magnesium.

Solid State Processing

Through solid state processing metal matrix composites can be developed with the bond between metal matrix and dispersed phase because of the mutual diffusion among them in the solid state with the elevated temperature and pressure. The main fabrication methods for solid state processing of metal matrix composites are powder blending and consolidation, and physical vapor deposition.

Vacuum/gas sintering

The good controllability and broad list of properties have made vacuum and gas pressure sintering, which is the most preferred sintering technique (Xiong *et al.*, 2018). This technique is very similar to high-energy ball milling and sintering, the contrast exists only next to compacting. Gao *et al.* observed that the alloys possess the minimum porosity, uniform microstructure, excellent mechanical and damping properties (Gao *et al.*, 2017) when the sintering temperature is raised to a particular temperature.

Powder blending and consolidation

Metal alloy powder is blended with ceramic whisker/short fiber/particles in dry condition. After blending, the mixture is further processed by cold compaction. These blended powders were uniaxially compacted to obtain billets of 36 mm in diameter and 40 mm in height at a pressure of ~100 bar. The green compacted billets were then subjected to sintering. Prior to hot extrusion, the compacted billets were homogenized at 400°C for 1 h and subsequently extruded at 350°C using a 150-ton hydraulic press to obtain cylindrical rods of ~7–10 mm in diameter. The extruded rods were used for characterization and testing. This method is usually used for the processing of aluminum and magnesium metal matrix composites. The schematic of the preparation process was pictured in Fig. 3.

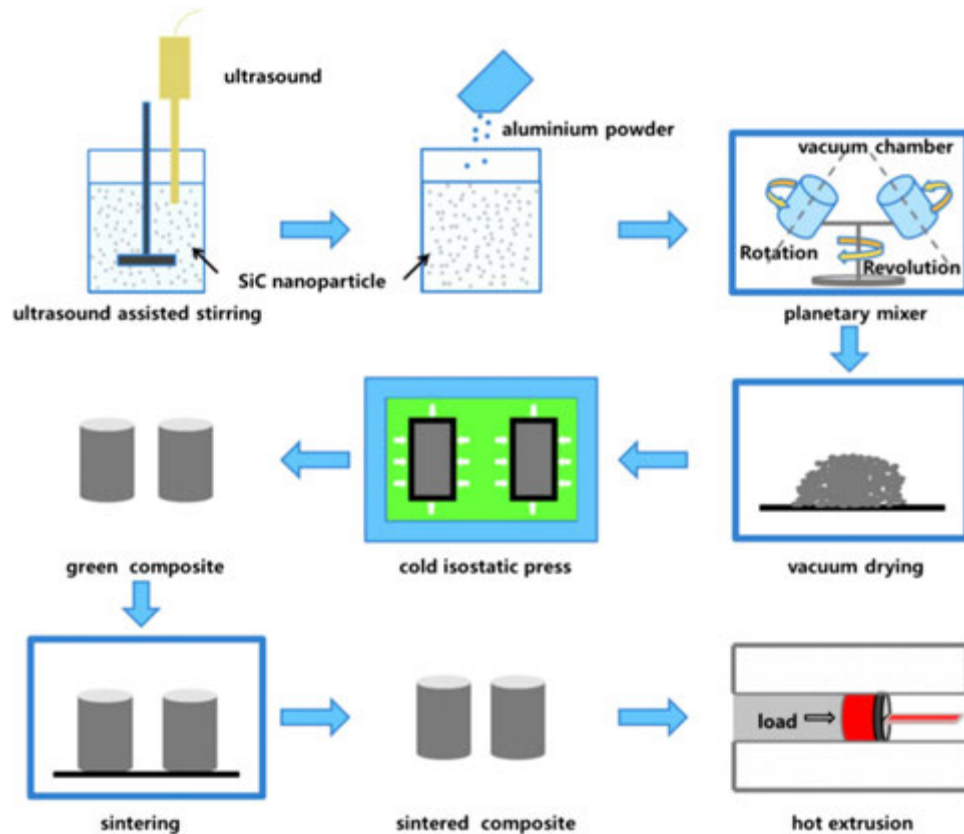


Fig. 3 Schematic illustration of the preparation of composites using powder blending and consolidation. Reproduced from Zeng, X., Liu, W., Xu, B., Shu, G., Li, Q., 2018. Microstructure and mechanical properties of Al–SiC nanocomposites synthesized by surface-modified aluminium powder. *Metals* 8 (4). Available at: <https://doi.org/10.3390/met8040253>.

Diffusion bonding

This is a well-known solid-state processing technique which combines same or varied metals. The bond is formed by inter diffusion of atoms in clean metallic surfaces, with elevated temperature. The inter diffusion atoms at the metallic surfaces under pressure creates bonding between the metal matrix and reinforcements (Kandpal *et al.*, 2014). This fabrication method is widely used for aluminum or magnesium MMCs reinforced with continuous/discontinuous fibers.

In-Situ Processing

In-situ processing involves chemical reactions which result in the creation of reinforcing phase within a metal matrix (Sastry *et al.*, 2001; Shunmugasamy *et al.*, 2016; Zhang *et al.*, 1993). The reinforcements can be formed from the precipitation in liquid or solid. A fine and well distributed reinforcement have been developed by this process. In between the matrix and the reinforcing phase, a fine bonding was evolved. They have grabbed much attention by its significantly low fabrication cost and output is huge (Nukami and Flemings, 1995; Premkumar and Chu, 1995). Fig. 4 displays the fabrication of as-cast TiB₂/AZ91 composite by stir casting method. Cao *et al.* (Xiao *et al.*, 2020) studied the damping characteristics of TiC reinforced to Mg metal matrix composites. With the increase of volume percentage of TiC particles, the damping capabilities of TiC/AZ91D composite have also been enhanced.

Damping Characteristics of Mg and Al-Based MMCs

In the field of semiconductor accessories, defense and aerospace, the priority of the light weight metallic materials i.e., Al and Mg have been rapidly raised in making the mechanical systems. The lower density of Mg (1.74 g/cc) than Al (2.7 g/cc) and the static stiffness of Mg (40 GPa) less than that of Al (70 GPa) have emerged Magnesium (Mg) as a most preferred light weight metallic materials (Gupta and Sharon, 2010; Matli *et al.*, 2020). Besides, the ability of exhibiting good damping characteristics than all other light weight metallic materials of Mg has helped dissipating the stored strain energy in the equipment's (Anilchandra and Surappa, 2012). Here, the improved inherent stiffness and damping capacities that enhanced the applications of Mg and Al matrix composites in the different engineering fields.

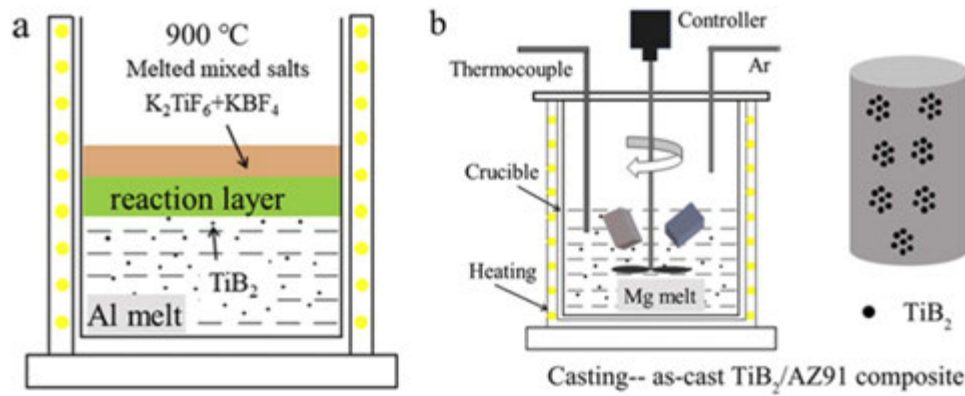


Fig. 4 Schematic of fabricating the In-situ Al-TiB₂ nanocomposite.

The anti-vibration capability of a material can be demonstrated with the damping capacity. The stability of the instrument and improvement of vehicle can be attained by the unwanted mechanical vibration and noise in the high damping materials. Pure Mg exhibit remarkably high damping capacity, whereas the vast applications of the pure Mg have been prevented by its low-tensile strength and elastic modulus. So, the Mg-MMC possessing better mechanical performance and high damping capacity parallel was the main motto of this extensive research. The high damping capacity can be attained by Magnesium matrix and the high mechanical strength can be obtained by the reinforcements (Xiuqing *et al.*, 2007).

The capability of a material to suppress or prevent the vibrations is called as its vibration damping. This vibration energy was observed by the material and gets utilized in various other forms of energy such as heat energy etc. The resonating frequencies that were the functions of the material properties such as elasticity, density and its microstructure have a frequency spectrum to these vibrations. The general representation of a sinusoidal damped vibration equation (Manakari *et al.*, 2017) is as follows Eq.

$$y(t) = Ae^{-kt} \sin(\omega t + \Phi)$$

where t is the time; A is the initial amplitude; k represents the decay constant which is material dependent property; ω is the angular frequency; Φ is the phase angle; and frequency; f is the number of cycle per time unit equals $\omega/2\pi$. Damping factor is estimated as,

$$Q^{-1} = k/\pi f$$

Damping loss rate is a function of sample weight (m) and the average ratio of two adjacent peaks from amplitude-time plot. The below equation represents the damping loss rate:

$$\partial = \frac{1}{m} \ln \left(\frac{y_1}{y_2} \right)$$

The damping tests have been carried out on Mg or Al-based metal matrix composites using the resonant frequency and damping analyzer (ICME, Belgium). The results were presented and discussed in this article.

Damping Characteristics of Mg-Based MMCs

Kumar *et al.* (2017) studied the role of La on the microstructural and damping properties of Mg-3Al alloy composites prepared by disintegrated metal deposition (DMD) technique followed by hot extrusion. Fig. 5 shows the damping characteristics of extruded pure Mg and Mg-3Al-xLa ($x \sim 1, 2.5, 4$) alloys.

They concluded that the increase in the amount of Al, the damping properties of pure Mg have declined. Whereas with the addition of (1, 2.5, 4) La, the damping capacity of Mg-3Al alloys was increased. The presence of La (2.5%) exposed there is an enhancement in the damping of Mg-3Al alloy by the damping measurement. The addition of 3Al, 3Al-1La, and 3Al-4 La has decreased the damping loss rate. When compared to pure Mg, a little enhancement in the damping loss rate was in the 3Al-2.5La. A minimum time is taken for suppressing the vibrations by Mg-3Al-2.5La is concluded from the damping results. The addition of La has played a key role in enhancing the damping performance of Mg-3Al alloy.

Nguyen *et al.* (2015) developed Mg- Al₈₅Ti₁₅ composites using rapid microwave sintering assisted powder metallurgy technique. The damping properties of the Mg- Al₈₅Ti₁₅ have been examined for the first by them and the data tabulated in Table 1. Fig. 6 shows the damping characteristics of pure Mg and it's composites. The significant enhancement in the damping properties of Mg by the adding of Al₈₅Ti₁₅ metastable powder particles can be concluded from the obtained results. With the increased amount of particles there was a slight reduction in the resonant frequency but the resonant frequency for the pure Al is observed to be 4620 Hz. The Mg-9Al₈₅Ti₁₅ composites exhibit a damping loss rate of 30 which is 3.75 times of pure Mg that is 8. A collaborative role has been played by the various damping mechanism such as twinning, microstructural defects and thermal mismatch.

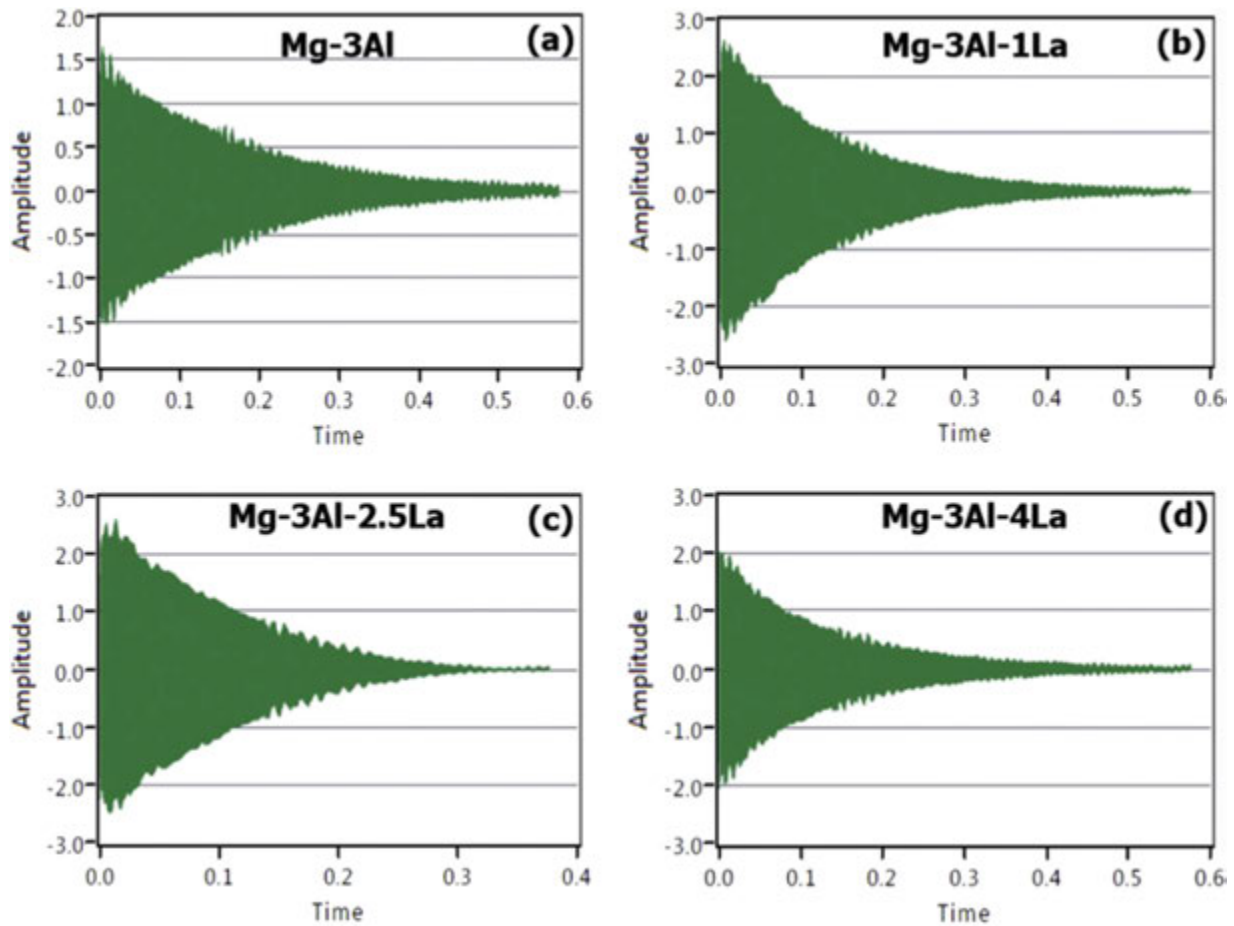


Fig. 5 Damping properties of Mg-3Al and Mg-3Al-xLa ($x = 1, 2.5, 4$) alloys.

Wakeel *et al.* (2018) fabricated Mg-NiTi nanocomposite using the microwave sintering assisted powder metallurgy technique. The final values of damping and elastic modulus of the fabricated materials were represented in the Table 1. The addition of NiTi particles has enhanced its damping loss rate. Whereas the damping capacity of the Mg-2NiTi nanocomposite have obtained a value near to 21 that was 2.6 times higher when compared with the pure Mg. The damping capacity of the Mg-2NiTi nanocomposite attained significant improvement (with a value of 0.0008) that was 119% higher than the pure Mg. By introducing the NiTi SMA nanoparticles have attained a considerable enhancement in the damping characteristics of the pure Mg.

Gururaj *et al.* (Parande *et al.*, 2016) examined the damping characteristics and microstructure of Mg-SiO₂ nanocomposites using the assistance of hybrid powder metallurgy technique. Table 1 listed the damping characteristics of pure Mg and Mg-SiO₂ nanocomposites. The damping properties of the pure Mg have been enhanced significantly with the addition of SiO₂ nanoparticles. There is an enhancement in the damping loss rate by the addition of SiO₂ NPs. The maximum value of damping loss rate of *64 (*7 times of the pure Mg) has been possessed by the Mg-2 vol% SiO₂ nanocomposites.

Gururaj *et al.* (Parande *et al.*, 2018) developed Mg- β -tricalcium phosphate composites via hybrid powder metallurgy method. The damping characteristic of pure Mg and Mg vol%-TCP composites was represented in Fig. 7.

The elastic modulus, damping capacities and damping loss rate of the composite samples can be known from Table 1. As the amount of β -TCP increased the damping loss rate (L) and the damping capacity (Q^{-1}) enhanced. The best values for damping loss rate (L) and the damping capacity (Q^{-1}) is attained with Mg-1.5 TCP are ~ 17.7 and $\sim 7.59 \times 10^{-4}$, respectively, which was $\sim 109\%$ and $\sim 15.7\%$ to that of pure Mg.

Sravya *et al.* (Tekumalla *et al.*, 2019) fabricated E21-B4C composite by disintegrated melt deposition phenomenon and hot extrusion. They reported that there was no significant variation in the damping capacity and Young's modulus with respect to E21-1.5B4C Mg alloy whereas in the context of E21-2.5B4C Mg alloys a marginal increase was observed in the damping capacity and Young's modulus. From the above, we can conclude that the E21-2.5B4C nanocomposites possess the highest Young's modulus and best damping capacity. This attains lots of applications to thus nanocomposites in the suitable aircraft applications in addition to the present seat frames.

The effects of presence of SiC particulate reinforcement in Mg matrix have been examined by Srikanth *et al.* (Narasimalu and Gupta, 2006). The overall damping capacity of the ductile metallic matrix have enhanced with the inclusion of hard reinforcing particulates that can be concluded from the studies.

Table 1 Damping characteristics of Mg based composites

Composition	Processing method	Damping capacity ($\times 10^{-4}$)	Damping loss rate	Elastic modulus (GPa)
Pure Mg	DMD + HE (Kumar <i>et al.</i> , 2017)	8.00 ± 1.000	0.000456	–
Mg-3Al		6.16 ± 0.377	0.000204	–
Mg-3Al-1La		7.13 ± 0.185	0.000245	–
Mg-3Al-2.5La		8.29 ± 0.827	0.000265	–
Mg-3Al-4La		6.73 ± 0.311	0.000217	–
Pure Mg	PM + MWS + HE (Kujur <i>et al.</i> , 2018)	3.94 ± 0.21	8.2 ± 0.2	42.3 ± 0.14
Mg0.5CeO ₂		11.06 ± 0.13 ($\uparrow 180.7\%$)	27.4 ± 0.3 (*3.34)	42.7 ± 0.01 ($\uparrow 0.95\%$)
Mg1.0CeO ₂		13.97 ± 0.2 ($\uparrow 254.5\%$)	31.3 ± 0.4 (*3.81)	43.4 ± 0.19 ($\uparrow 2.6\%$)
Mg1.5CeO ₂		18.97 ± 1.2 ($\uparrow 381.5\%$)	40.9 ± 2.7 (*4.98)	43.9 ± 0.02 ($\uparrow 3.8\%$)
Pure Mg	PM + MWS + HE (Kujur <i>et al.</i> , 2017)	3.94 ± 0.21	8.2 ± 0.2	42.3 ± 0.14
Mg-0.5 Sm ₂ O ₃		7.19 ± 0.17 ($\uparrow 82.48\%$)	20.2 ± 0.4 (*2.46)	43.7 ± 0.1 ($\uparrow 3.30\%$)
Mg-1 Sm ₂ O ₃		10.49 ± 0.58 ($\uparrow 166.24\%$)	29.35 ± 1.2 (*3.57)	45.4 ± 0.08 ($\uparrow 7.32\%$)
Mg-1.5 Sm ₂ O ₃		11.39 ± 0.8 ($\uparrow 189.21\%$)	36.65 ± 0.9 (*4.47)	44.9 ± 0.2 ($\uparrow 6.14\%$)
Pure Mg	PM + MWS + HE (Parande <i>et al.</i> , 2016)	6.56 ± 0.23	8.3 ± 0.2	44.7 ± 0.20
Mg-0.5SiO ₂		12.79 ± 0.11	35.8 ± 0.8	45.3 ± 0.65
Mg-1SiO ₂		19.68 ± 0.45	55.2 ± 0.6	46.7 ± 0.31
Mg-2SiO ₂		22.29 ± 0.06	63.9 ± 1.3	45.6 ± 0.58
Pure Mg	DMD + HE (Nguyen <i>et al.</i> , 2015)	7.15 ± 0.45	8 ± 1	–
Mg-3Al ₈₅ Ti ₁₅		17.15 ± 0.10	25 ± 2 (+212%)	–
Mg-6Al ₈₅ Ti ₁₅		22.84 ± 0.14	28 ± 2 (+250%)	–
Mg-9Al ₈₅ Ti ₁₅		25.63 ± 0.18	30 ± 2 (+275%)	–
Pure Mg	DMD + HE (Manakari <i>et al.</i> , 2017)	5.46 ± 0.32	8.6 ± 0.4	43.3 ± 0.16
Mg-5GMB		9.8 ± 0.17	31.2 ± 0.7	42.56 ± 0.28
Mg-15GMB		16.31 ± 0.42	67.3 ± 1.9	41.10 ± 0.18
Mg-25GMB		25.60 ± 0.50	108.2 ± 2.3	39.85 ± 0.12
Pure Mg	PM + MWS + HE (Wakeel <i>et al.</i> , 2018)	3 ± 0.2	8 ± 0.2	42.3 ± 0.14
Mg-2NiTi		8 ± 0.5	21 ± 2	45 ± 0.1
Pure Mg	PM + MWS + HE (Parande <i>et al.</i> , 2018)	6.56 ± 0.2	8.3 ± 0.2	44.7 ± 0.2
Mg-0.5TCP		6.94 ± 0.2 ($\uparrow 5.7\%$)	15.7 ± 0.9 ($\uparrow 89\%$)	43.7 ± 0.4
Mg-1.0 TCP		6.96 ± 0.3 ($\uparrow 6.0\%$)	17.4 ± 0.7 ($\uparrow 109\%$)	43.5 ± 0.08
Mg-1.5 TCP		7.59 ± 0.2 ($\uparrow 15.7\%$)	17.7 ± 0.5 ($\uparrow 113\%$)	43.7 ± 0.6
Mg2.5Zn	DMD + HE (Parande <i>et al.</i> , 2020)	9.59 ± 0.03	17.4 ± 2.0	46.12 ± 0.5
Mg2.5Zn-3ES		12.79 ± 0.06 ($\uparrow 33.3\%$)	35.8 ± 2.1 ($\uparrow 105.7\%$)	46.89 ± 0.8
Mg2.5Zn-5ES		17.68 ± 0.08 ($\uparrow 84.3\%$)	43.1 ± 3.7 ($\uparrow 147.7\%$)	47.65 ± 0.1
Mg2.5Zn-7ES		19.68 ± 0.12 ($\uparrow 105.2\%$)	55.0 ± 2.6 ($\uparrow 216.1\%$)	48.1 ± 1.2

Mili *et al.* (Kujur *et al.*, 2017) developed Sm₂O₃ nanoparticles reinforced Mg composites using hybrid microwave sintering and hot extrusion. The amplitude-time plots of respective samples have been represented in Fig. 8. The characteristics of the pure Mg and its composites such as damping capacity, damping loss rate and elastic module were listed in the Table 1.

With the increase in the amount of Sm₂O₃ NPs, the damping capacities and the damping loss rate of pure Mg have been enhanced. A significant increase in the damping capacity was achieved with the inclusion of Mg-1.5 vol% Sm₂O₃ (which is ~4.5 times that of a pure Mg). The Mg-Sm₂O₃ composites exhibiting damping properties with nearly same elastic modulus of the human bone made it as an efficient for implant material.

Vyasraj *et al.* (Manakari *et al.*, 2017) synthesized hollow glass microspheres (5, 15 and 25 wt%) reinforced magnesium composites using the disintegrated melt deposition (DMD) method and studied its damping properties. The ability of a material to absorb vibration can be known as damping loss rate (L), which is showed an increase with the addition of glass microspheres (Fig. 9a). Damping loss rate of Mg-25 composite increased by 12.5 times when compared to pure Mg and exhibited a linear relationship with increasing amount of reinforcement.

Damping capacity of Mg-25 composite increased by 370% when compared to pure Mg and exhibited a linear relationship with increasing amount of reinforcement. Damping capacity (Q^{-1}) of Mg also seen to be increasing with the increasing filler loadings (Fig. 9b).

Damping Characteristics of Al-Based MMCs

In general, the damping capacity possessed by Al was comparatively low. Through the thermal mismatch strain induction, the matrix microstructure including reinforcement and dislocation in the matrix were attained by MMC fabrication techniques.

The microstructural and damping response of Al-NiTi nanocomposites have been investigated by Penchal *et al.* (Matli *et al.*, 2020) using microwave with the assistance of two-directional rapid sintering and hot extrusion successively. The amorphous Ni₅₀Ti₅₀ reinforcement (0.5%, 1% and 1.5 Vp.%) materials and the Al matrix are the requirements for this process. A composite

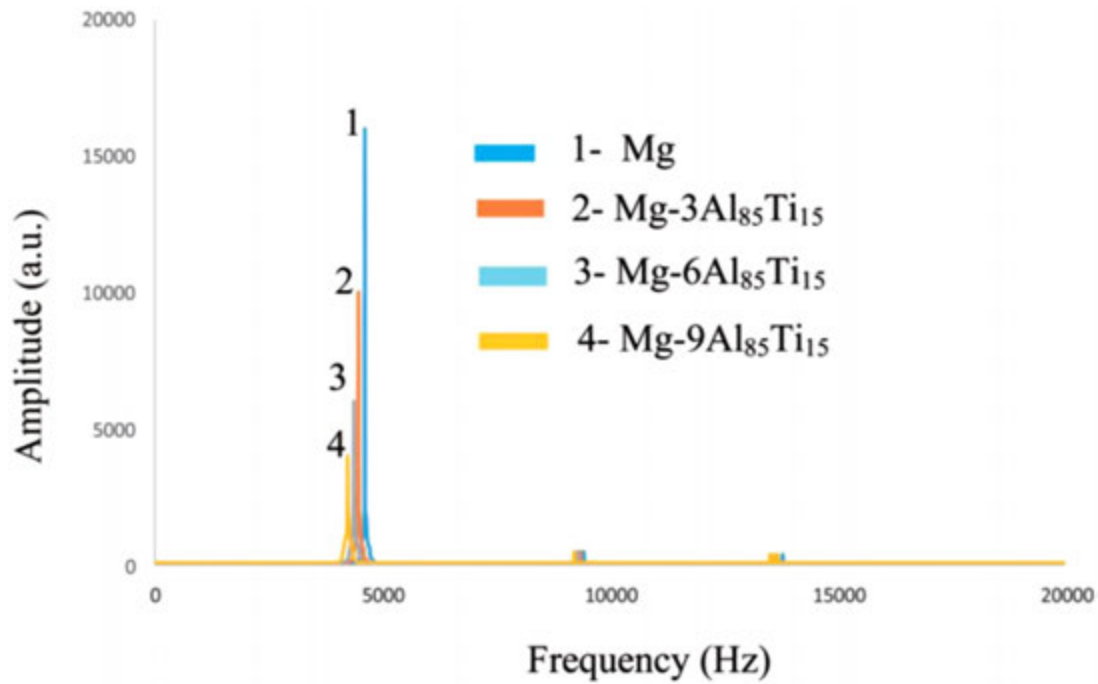


Fig. 6 Resonant frequency of pure magnesium and its composite samples.

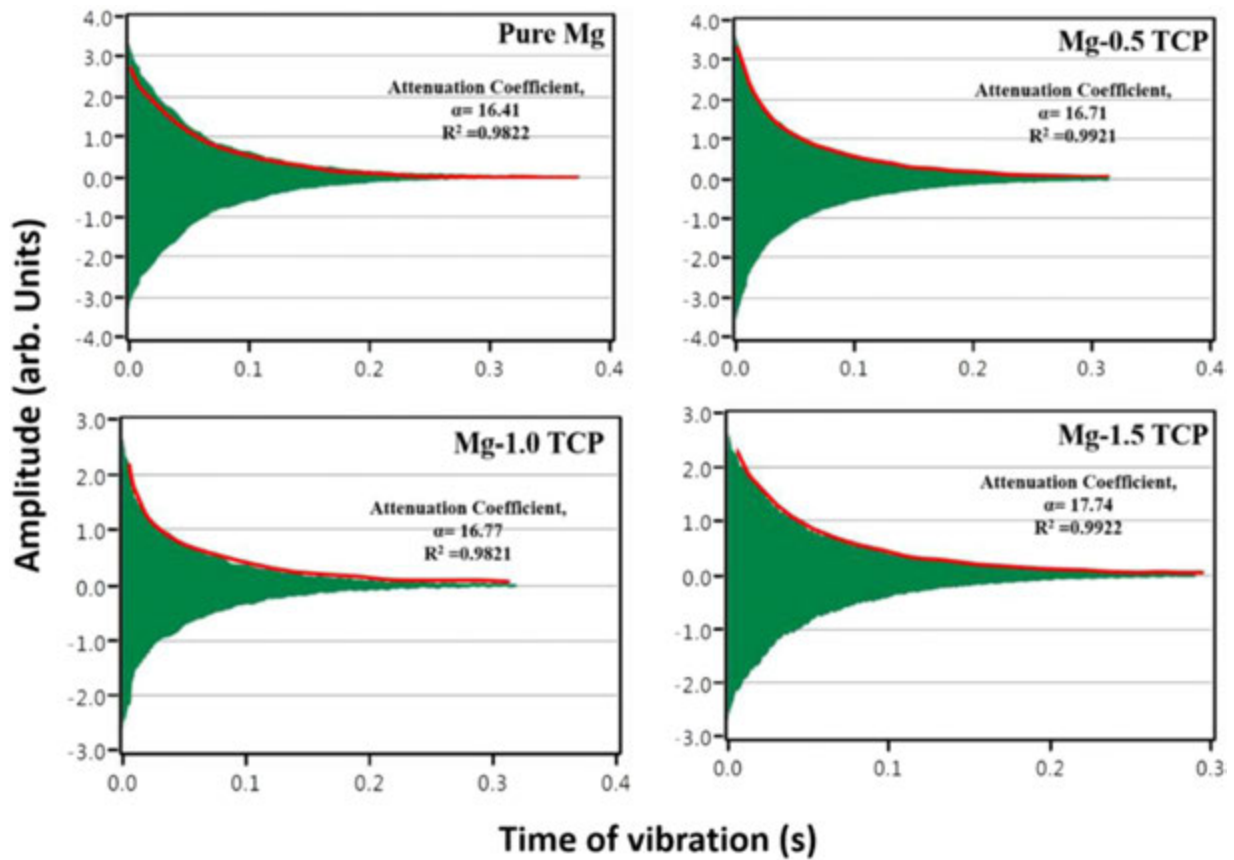


Fig. 7 Damping characteristics of pure magnesium and Mg- β -TCP composites.

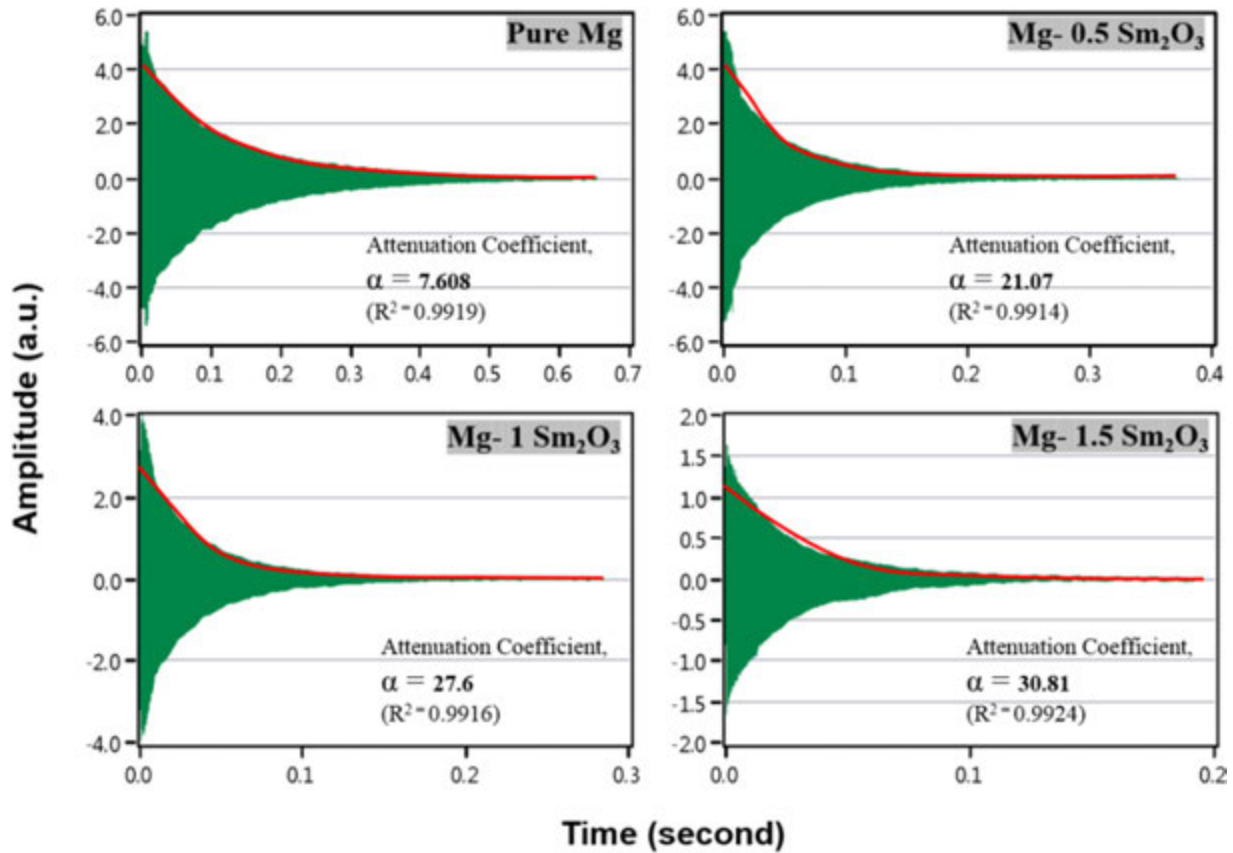


Fig. 8 Damping characteristics of Mg- Sm_2O_3 nanocomposites.

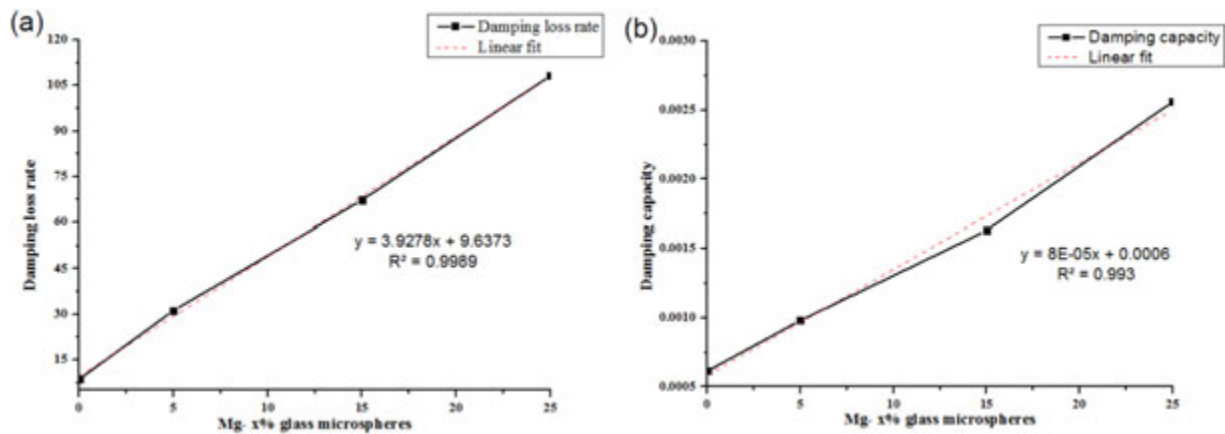


Fig. 9 Linear fitted curves for: (a) Damping loss rate, and (b) Damping capacity as a function of GMB content.

powder was fabricated by ball milling the prepared powders for 120 min at a speed of 200 rpm. At a compaction pressure of 97 bar (50 tons), blended powders were compressed. A cylindrical billet of 40 mm and 35 mm diameter is acquired. At a temperature of 550°C, through hybrid microwave set-up the compacted billets were sintered. To produce an extruded rod of 8 mm diameter, the sintered billet was hot extruded at 350°C at an extrusion ratio of 20.25:1.

Through the resonance frequency damping analyzer (RFDA) the damping property measurements was conducted. Fig. 10 and Table 2 represents the Vibration damping capabilities of pure Al and Al-NiTi nanocomposites. With the incorporation of NiTi nanoparticles greater/equal to one volume percent, the damping capacity (Q^{-1}) and the damping loss rate (L) of the pure Al were found be enhanced significantly. The optimum values of damping capacity and damping loss rate at ~ 6.15 and $\sim 17.15 \times 10^{-4}$, were acquired for Al-1.5 NiTi nanocomposite were obtained respectively in this investigation. When compared to pure Al, the damping capacity and damping loss rate for the nanocomposite sample was enhanced by $\sim 15.4\%$ and $\sim 16.2\%$.

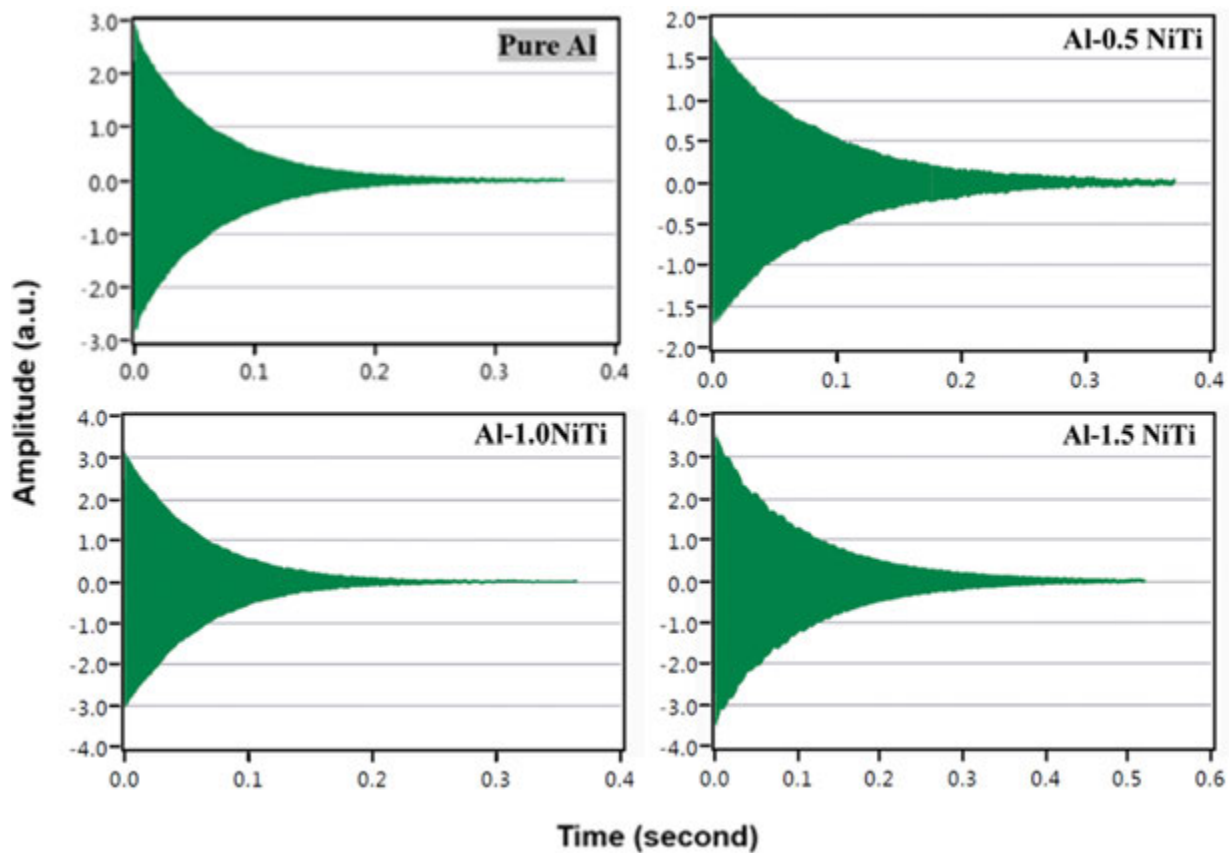


Fig. 10 Damping characteristics of Al- $\text{Ni}_{50}\text{Ti}_{50}$ nanocomposites.

Penchal Reddy *et al.* (2018) studied the Al/BN nanocomposites can be developed by two-directional microwave assisted rapid sintering. The processing details were similar to earlier studies in Penchal *et al.* (Matli *et al.*, 2020). The amplitude-time plot of pure Al and Al-BN nanocomposite specimens was represented in Fig. 11.

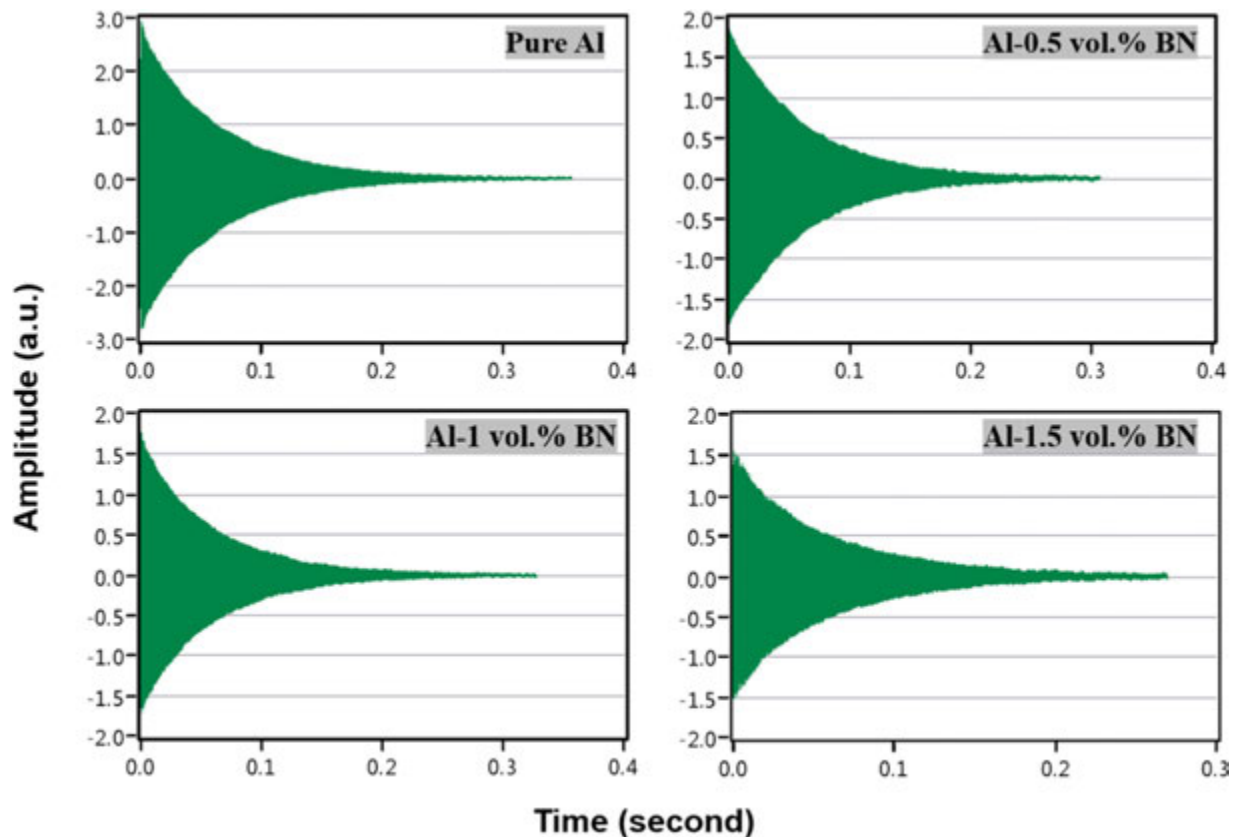
The damping properties of pure Al and its Al-BN (0.5, 1 and 1.5 vol%) nanocomposites were tabulated in Table 2. In the free vibration mode, every specimen's vibration response obtained is factor of time and amplitude. The results conclude that for every material, there is a varied amplitude and different time taken by vibration to prevent the amplitude. The damping characteristics of the pure Al have been increased by the inclusion of nano-BN particulates as reinforcement. Fig. 11 concludes that there is a sudden decline in the amplitude of Al-BN nanocomposites whereas pure Al has a periodic fall in the amplitude. Vibrations are damped in less than ~ 0.27 s for Al-1.5 vol% BN nanocomposite. The gradually addition of nano-BN particulates have resulted with a dominant improvement in the damping capacity (Q^{-1}). The Al-1.5 vol% BN nanocomposite gave a maximum damping capacity of 0.000676 (which is 26.8 times that of pure Al). Then, the resonant frequency for pure Al was found to be 8846 Hz whereas the addition of nano-BN particulates with varied vol% such as (0.5, 1.0 and 1.5) BN nanocomposite resulted in a slight decrease of the resonant frequency, the values were found to be 8573, 8528 and 8492 Hz, respectively. When compared to pure Al, the benefits such as reduced resonant frequency and vibration amplitude have led to overall damping capacity of the nanocomposites. Fig. 12.

Through Disintegrated deposition method (DMD) technique, Narasimalu *et al.* (Narasimalu and Gupta, 2006) investigated the damping behavior of Al (AA1050) alloy-SiC composites. The results concluded that there is an overall enhancement in the damping capacity of Al matrix with the addition of SiC ($\sim 25 \mu\text{m}$ size) to the matrix and presence of interconnected Fe wire. The presence of Al with 0.5 vol% of SiC and 2 vol% of interconnected Fe wire, jointly exhibits a damping capacity 25% higher than that of pure Al, whereas interconnected Fe wire lonely provides only 15% higher than that of pure Al and there was a 10% variation when compared with SiC particulates and Fe wire. So, the presence of both SiC particulates and Interconnected incorporates to attain the best damping capacity to the Al.

Madeira *et al.* (2016) studied Al composites reinforced with SiC particles. The result reports that the particle size and the frequency were directly proportional to the damping capacity whereas the particle size decreases the dynamic modulus. Zhang *et al.* (1994) studied 6061 Al/SiC and 6061 Al/Gr composites and compared with that of Al alloy. This study concluded that the damping capacity was enhanced with the reinforced composites unlike unreinforced alloys. The damping capacity of the graphite reinforcement is volume fraction dependent, whereas SiC is volume fraction independent.

Table 2 Damping characteristics of Al based composites

Composition	Processing method	Damping capacity ($\times 10^{-4}$)	Damping loss rate	Elastic modulus (GPa)
Pure Al	PM + MWS + HE (Matli <i>et al.</i> , 2020)	5.33 ± 0.056	14.76 ± 0.09	71.65 ± 0.02
Al-0.5 vol% NiTi		4.17 ± 0.031 ($\downarrow 21.7\%$)	11.65 ± 0.06 ($\downarrow 21\%$)	75.99 ± 0.02 ($\uparrow 6.05\%$)
Al-1.0 vol% NiTi		5.65 ± 0.029 ($\uparrow 6\%$)	15.2 ± 0.06 ($\uparrow 2.98\%$)	76.48 ± 0.01 ($\uparrow 6.74\%$)
Al-1.5 vol% NiTi		6.15 ± 0.029 ($\uparrow 15.4\%$)	17.15 ± 0.06 ($\uparrow 16.19\%$)	75.93 ± 0.08 ($\uparrow 5.97\%$)
Al-0.5 vol% BN	PM + MWS + HE (Penchal Reddy <i>et al.</i> , 2018)	5.88 ± 0.073 ($\uparrow 10.3\%$)	15.78 ± 0.11 ($\uparrow 6.91\%$)	71.88 ± 0 ($\uparrow 0.32\%$)
Al-1.0 vol% BN		6.18 ± 0.039 ($\uparrow 15.9\%$)	16.48 ± 0.09 ($\uparrow 11.65\%$)	72.2 ± 0.006 ($\uparrow 0.76\%$)
Al-1.5 vol% BN		6.76 ± 0.042 ($\uparrow 26.8\%$)	18.3 ± 0.07 ($\uparrow 24\%$)	73.08 ± 0.017 ($\uparrow 2\%$)

**Fig. 11** Damping characteristics of pure Al and Al-BN nanocomposites.

Summary and Conclusions

The main aim of the current article was to draw the attention among the damping characterization and the fabrication processes of the MMCs in addition to product application. The following are the respective conclusions from this article:

- (1) In this article, we have briefly gone through most commonly used fabricating techniques to manufacture MMCs, in which DMD and PM were mostly employed. In the enrichment of damping properties, Secondary fabrication process such as extrusion was employed successfully.
- (2) The types of matrix, reinforcements (individual, multiple, percentage, size, distribution in matrix), wettability and reaction during the fabrication process were the factors influencing the damping characteristics of the matrix.
- (3) During the past few decades, there were several studies was competed on Mg and Al MMCs to attain a conclusion and introducing them in the progressively developed industries. To acquire the complete knowledge on the collaboration of processing route, microstructure, and damping properties, a great research has been done.

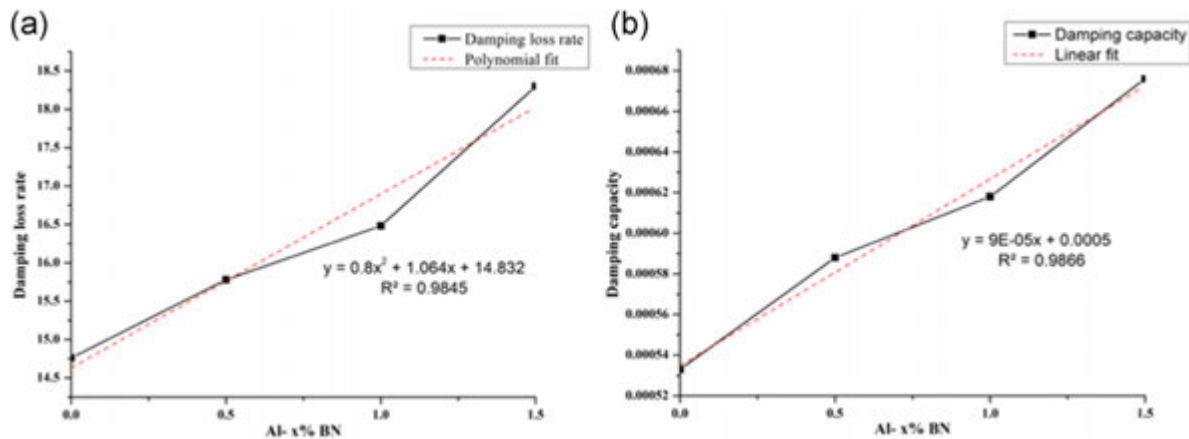


Fig. 12 Fitted curves for: (a) Damping loss rate, and (b) Damping capacity as a function of amount of reinforcement (BN).

- (4) In the fields of space technology, aircraft industry, automobile component, electrical and electronic field, and other product applications, the demand for usage of MMCs have prominently enhanced. Besides, to examine the MMCs usage in the context of cost and good performance, they reported that an exclusive research is required.

References

- Anilchandra, A.R., Surappa, M.K., 2012. Microstructure and damping behaviour of consolidated magnesium chips. *Materials Science and Engineering A* 542, 94–103. <https://doi.org/10.1016/j.msea.2012.02.038>.
- Davis, L.C., Artz, B.E., 1995. Thermal conductivity of metal-matrix composites. *Journal of Applied Physics* 77 (10), 4954–4960. <https://doi.org/10.1063/1.359302>.
- Gao, Y., Luo, B.-H., He, K., *et al.*, 2017. Mechanical properties and microstructure of WC-Fe-Ni-Co cemented carbides prepared by vacuum sintering. *Vacuum* 143, 271–282. <https://doi.org/10.1016/j.vacuum.2017.06.028>.
- Gupta, M., Wong, W.L.E., 2015. Magnesium-based nanocomposites: Lightweight materials of the future. *Materials Characterization* 105, 30–46. <https://doi.org/10.1016/j.matchar.2015.04.015>.
- Gupta, M., Sharon, N.M.L., 2010. *Magnesium, Magnesium Alloys, and Magnesium Composites*. Wiley. <https://doi.org/10.1002/9780470905098>.
- Gupta, N., Luong, D.D., Cho, K., 2012. Magnesium matrix composite foams—density, mechanical properties, and applications. *Metals* 2 (3). <https://doi.org/10.3390/met2030238>.
- Ibrahim, I.A., Mohamed, F.A., Lavernia, E.J., 1991. Particulate reinforced metal matrix composites – A review. *Journal of Materials Science* 26, 1137–1156. <https://doi.org/10.1007/BF00544448>.
- Kandpal, B.C., Kumar, J., Singh, H., 2014. Production technologies of metal matrix composite: A review. *International Journal of Research In Mechanical Engineering & Technology* 4 (2), (5762).
- Kujur, M.S., Mallick, A., Manakari, V., *et al.*, 2017. Significantly enhancing the ignition/compression/damping response of monolithic magnesium by addition of Sm_2O_3 nanoparticles. *Metals* 7 (9), 357. <https://doi.org/10.3390/met7090357>.
- Kujur, M.S., Manakari, V., Parande, G., *et al.*, 2018. Enhancement of thermal, mechanical, ignition and damping response of magnesium using nano-ceria particles. *Ceramics International* 44 (13), 15035–15043. <https://doi.org/10.1016/j.ceramint.2018.05.133>.
- Kumar, A., Meenashisundaram, G.K., Manakari, V., Parande, G., Gupta, M., 2017. Lanthanum effect on improving CTE, damping, hardness and tensile response of Mg-3Al alloy. *Journal of Alloys and Compounds* 695, 3612–3620. <https://doi.org/10.1016/j.jallcom.2016.11.400>.
- Li, P.Y., Dai, S.L., Chai, S.C., Li, Y.R., 2000. High damping Al-Fe-Mo-Si/Zn-Al composites produced by rapidly solidified powder metallurgy process. *Scripta Materialia* 42, 955–960.
- Lu, H., Wang, X., Zhang, T., Cheng, Z., Fang, Q., 2009. Design, fabrication, and properties of high damping metal matrix composites—a review. *Materials* 2 (3). <https://doi.org/10.3390/ma2030958>.
- Madeira, S., Carvalho, O., Carneiro, V.H., *et al.*, 2016. Damping capacity and dynamic modulus of hot pressed AlSi composites reinforced with different SiC particle sized. *Composites Part B Engineering* 90, 399–405. <https://doi.org/10.1016/j.compositesb.2016.01.008>.
- Manakari, V., Parande, G., Doddamani, M., Kumar, G., 2017. Enhancing significantly the damping response of Mg using hollow glass microspheres while simultaneously reducing weight. *Advanced Materials Letters* 8 (12), 1171–1177. <https://doi.org/10.5185/amlett.2017.1697>.
- Matli, P.R., Manakari, V., Parande, G., *et al.*, 2020. Improving mechanical, thermal and damping properties of NiTi (Nitinol) reinforced aluminum nanocomposites. *Journal of Composites Science* 4 (1), 19. <https://doi.org/10.3390/jcs4010019>.
- Miracle, D.B., 2005. Metal matrix composites – From science to technological significance. *Composites Science and Technology* 65, 2526–2540. <https://doi.org/10.1016/j.compscitech.2005.05.027>.
- Narasimalu, S., Gupta, M., 2006. Effect of the presence of continuous/ discontinuous/hybrid reinforcement on the damping characteristics of pure aluminium matrix. *Solid State Phenomena* 111, 71–74. <https://doi.org/10.4028/www.scientific.net/SSP.111.71>.
- Nguyen, Q.B., Nai, M.L.S., Nguyen, A.S., *et al.*, 2015. Microstructure and damping characteristics of Mg and its composites containing metastable Al85Ti15 particle. *Journal of Composite Materials* 50 (18), 2565–2573. <https://doi.org/10.1177/0021998315608432>.
- Nukami, T., Flemings, M.C., 1995. In situ synthesis of TiC particulate-reinforced aluminum matrix composites. *Metallurgical and Materials Transactions A* 26.
- Parande, G., Manakari, V., Meenashisundaram, G.K., Gupta, M., 2016. Enhancing the hardness/compression/damping response of magnesium by reinforcing with biocompatible silica nanoparticles. *International Journal of Materials Research* 107 (12), 1091–1099. <https://doi.org/10.3139/146.111435>.
- Parande, G., Manakari, V., Gupta, H., Gupta, M., 2018. Magnesium- β -tricalcium phosphate composites as a potential orthopedic implant: A mechanical/damping/immersion perspective. *Metals* 8 (5). <https://doi.org/10.3390/met8050343>.
- Parande, G., Manakari, V., Sharma Koppa, S.D., Gupta, M., 2020. A study on the effect of low-cost eggshell reinforcement on the immersion, damping and mechanical properties of magnesium–zinc alloy. *Composites Part B Engineering* 182, 107650. <https://doi.org/10.1016/j.compositesb.2019.107650>.

- Penchal Reddy, M., Manakari, V., Parande, G., *et al.*, 2018. Enhancing compressive, tensile, thermal and damping response of pure Al using BN nanoparticles. *Journal of Alloys and Compounds* 762 (May), 398–408. <https://doi.org/10.1016/j.jallcom.2018.05.205>.
- Prasad, D.S., Shoba, C., Varma, K.R., 2015. Damping behavior of commonly used reinforcement powders – An experimental approach. *Engineering Science and Technology* 18 (4), 674–679. <https://doi.org/10.1016/j.jestch.2015.05.001>.
- Premkumar, M.K., Chu, M.G., 1995. Al/TiC particulate composite produced by a liquid state in situ process. *Materials Science and Engineering A* 202 (1), 172–178. [https://doi.org/10.1016/0921-5093\(95\)09787-2](https://doi.org/10.1016/0921-5093(95)09787-2).
- Rahiman, A.H.S., Smart, D.S.R., 2019. Damping characteristics of aluminium matrix composites – A review. *Materials Today: Proceedings* 11, 1139–1143. <https://doi.org/10.1016/j.matpr.2018.12.048>.
- Ramanathan, A., Krishnan, P.K., Muraliraja, R., 2019. A review on the production of metal matrix composites through stir casting – Furnace design, properties, challenges, and research opportunities. *Journal of Manufacturing Processes* 42, 213–245. <https://doi.org/10.1016/j.jmapro.2019.04.017>.
- Rawal, S., 2001. Metal-matrix composites for space applications. *JOM* 53, 14–17. <https://doi.org/10.1007/s11837-001-0139-z>.
- Sastry, S., Krishna, M., Uchil, J., 2001. A study on damping behaviour of aluminite particulate reinforced ZA-27 alloy metal matrix composites. *Journal of Alloys and Compounds* 314 (1), 268–274. [https://doi.org/10.1016/S0925-8388\(00\)01235-4](https://doi.org/10.1016/S0925-8388(00)01235-4).
- Schaller, R., 2003. Metal matrix composites, a smart choice for high damping materials. *Journal of Alloys and Compounds* 355 (1), 131–135. [https://doi.org/10.1016/S0925-8388\(03\)00239-1](https://doi.org/10.1016/S0925-8388(03)00239-1).
- S-de-la-Muela, A.M., Cambroner, L.E.G., Ruiz-Román, J.M., 2020. Molten metal infiltration methods to process metal matrix syntactic foams. *Metals* 10 (1). <https://doi.org/10.3390/met10010149>.
- Shunmugasamy, V.C., Mansoor, B., Gupta, N., 2016. Cellular magnesium matrix foam composites for mechanical damping applications. *JOM* 68 (1), 279–287. <https://doi.org/10.1007/s11837-015-1680-5>.
- Siva, D., Chintada, P., Dma, D.Á., Rice, Á., 2015. Damping behavior of metal matrix composites. *Transactions of the Indian Institute of Metals* 68, 161–167. <https://doi.org/10.1007/s12666-014-0462-z>.
- Srikanth, N., Gupta, M., 2001. Determination of energy dissipation in Mg/SiC formulations using a new method of suspended beam coupled with circle fit approach. *Scripta Materialia* 45 (9), 1031–1037. [https://doi.org/10.1016/S1359-6462\(01\)01131-9](https://doi.org/10.1016/S1359-6462(01)01131-9).
- Srikanth, N., Gaofeng, C.H., Gupta, M., 2003. Enhanced damping of a magnesium alloy by addition of copper. *Journal of Alloys and Compounds* 352 (1), 106–110. [https://doi.org/10.1016/S0925-8388\(02\)01131-3](https://doi.org/10.1016/S0925-8388(02)01131-3).
- Surappa, M.K., 2003. Aluminium matrix composites: Challenges and opportunities. *Sadhana* 28, 319–334. <https://doi.org/10.1007/BF02717141>.
- Tekumalla, S., Joo Yuan, N., Hagshenas, M., Gupta, M., 2019. Enhancing properties of aerospace alloy Elektron 21 using boron carbide nanoparticles as reinforcement. *Applied Sciences* 9 (24), 5470. <https://doi.org/10.3390/app9245470>.
- Wakeel, S., Manakari, V., Parande, G., *et al.*, 2018. Synthesis and mechanical response of NiTi SMA nanoparticle reinforced Mg composites synthesized through microwave sintering process. *Materials Today: Proceedings* 5 (14), 28203–28210. <https://doi.org/10.1016/j.matpr.2018.10.064>.
- Wu, G.H., Dou, Z.Y., Jiang, L.T., Cao, J.H., 2006. Damping properties of aluminum matrix–fly ash composites. *Materials Letters* 60 (24), 2945–2948. <https://doi.org/10.1016/j.matlet.2006.02.018>.
- Xiao, P., Gao, Y., Yang, C., *et al.*, 2020. Strengthening and toughening mechanisms of Mg matrix composites reinforced with specific spatial arrangement of in-situ TiB₂ nanoparticles. *Composites Part B: Engineering* 198, 108174. <https://doi.org/10.1016/j.compositesb.2020.108174>.
- Xiong, H., Wu, Y., Li, Z., *et al.*, 2018. Comparison of Ti(C, N)-based cermets by vacuum and gas-pressure sintering: Microstructure and mechanical properties. *Ceramics International* 44 (1), 805–813. <https://doi.org/10.1016/j.ceramint.2017.10.003>.
- Xiujing, Z., Haowei, W., Lihua, L., Naiheng, M., 2007. In situ synthesis method and damping characterization of magnesium matrix composites. *Composites Science and Technology* 67 (3), 720–727. <https://doi.org/10.1016/j.compscitech.2006.04.010>.
- Yang, K., Yang, X., He, C., *et al.*, 2017. Damping characteristics of Al matrix composite foams reinforced by in-situ grown carbon nanotubes. *Materials Letters* 209, 68–70. <https://doi.org/10.1016/j.matlet.2017.07.126>.
- Zhang, J., Perez, R.J., Lavernia, E.J., 1993. Documentation of damping capacity of metallic, ceramic and metal-matrix composite materials. *Journal of Materials Science* 28 (9), 2395–2404. <https://doi.org/10.1007/BF01151671>.
- Zhang, J., Perez, R.J., Lavernia, E.J., 1994. Effect of SiC and graphite particulates on the damping behavior of metal matrix composites. *Acta Metallurgica et Materialia* 42 (2), 395–409. [https://doi.org/10.1016/0956-7151\(94\)90495-2](https://doi.org/10.1016/0956-7151(94)90495-2).
- Zhang, X., Liao, L., Ma, N., Wang, H., 2006. Mechanical properties and damping capacity of magnesium matrix composites. *Composites Part A Applied Science and Manufacturing* 37 (11), 2011–2016. <https://doi.org/10.1016/j.compositesa.2005.12.007>.
- Zweben, C., 1992. Metal-matrix composites for electronic packaging. *JOM* 44 (7), 15–23. <https://doi.org/10.1007/BF03222270>.

Electromagnetic Shielding Capabilities of Metal Matrix Composites

Anisha Chaudhary and Vinay Gupta, University of Delhi, New Delhi, India

Satish Teotia, Khalifa University of Science & Technology, Abu Dhabi, United Arab Emirates

Subhash Nimanpure, Council of Scientific and Industrial Research, National Physical Laboratory, New Delhi, India

Dipen K Rajak, Sandip Institute of Technology and Research Centre, Nashik, Maharashtra, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

The advancement in the technology has changed our life, the manner in which we live, learn, communicate, travel and at the same time, simplified our life by saving time, improving communication, providing better health care services etc. Both our professional and personal life is extremely dependent on the advanced technology. The increasing use of communication technology and electrical/electronic devices has generated problems of electromagnetic radiation pollution (Yang *et al.*, 2018; Che *et al.*, 2004; Yang *et al.*, 2015; Song *et al.*, 2017). These undesired electromagnetic radiations not only affect the lifetime and performance of source electronic devices, but also interfere with the functioning of other nearby devices and create a problem of electromagnetic interference. Electromagnetic interference (EMI) is an undesired disturbance from the electromagnetic radiation that affects the normal functioning of the electrical circuits or devices. The sources of electromagnetic interference may be any natural or artificial objects that can generate radiated (electromagnetic waves) or conducted emission (noise). When a sensitive device comes in vicinity of the unwanted signal generated by certain other electrical or electronic circuit, disturbance in the form of EMI effect can be observed and these EMI disturbances may cause interruption, obstruction or complete degradation of the device performance (Zhang *et al.*, 2015b; Lee *et al.*, 2017b). Because of the reason of EMI, use of cell phone is limited inside an aeroplane or automated robotic operation theaters to avoid electronic failures. Moreover, the fast growth in scientific devices, military/aerospace instruments, industrial equipment, electronic and telecommunications system has developed a threat of EMI as the electromagnetic radiations are the leading cause of impairment in electronics, telecommunications, and aerospace components and devices. Therefore, need for a shielding mechanism arises to protect electronic devices from unwanted electromagnetic pollution and to make sure that device will work with other nearby electronic instruments without compromising the performance and disruption in device functioning.

This process of reducing the effect of electromagnetic radiation in a space with the help of some barrier or shield is called as EMI shielding. A significant reduction in electromagnetic fields, electrostatics fields and radio waves can be achieved with mechanism of shielding. Typically, shielding can be referred as an enclosure used to isolate the electronic device and its components from external radiations. Thus, shielding is the practice through which certain level of reduction in electromagnetic field can be achieved using specially designed shields. Materials used for shielding are called EMI shielding materials and the amount of reduction in electromagnetic fields largely depends on the properties of shielding materials used, the size and thickness of the shield and the interested frequency range etc (Thomassin *et al.*, 2007; Cho and Kim, 1999).

EMI Shielding Materials

The increased demand of advanced electronic devices and the serious threat from electromagnetic pollution has motivated the scientific community to develop EMI shielding materials that work in a broad electromagnetic frequency range. Current modern specialized gadgets operate in a wide frequency range having different EM bands. Each EM bands have characteristic applications. For example, wireless communications and earth orbit satellites work in L-band (1–2 GHz), for sound and sight applications such as TV, mobiles, cordless telephones etc, the S-band (2–4 GHz) is utilized, the C-band (4–8 GHz) is used in Wi-Fi devices and radio telecommunication, X-band (8–12 GHz) finds applications in civil, military and aerospace industries for defense tracking, weather monitoring, air traffic control and speed detection of vehicles and the Ku-band (12–18 GHz) band is employed as a part of very small aperture terminal systems (Kumar *et al.*, 2015; Belov *et al.*, 2012). Thus, depending upon the specific applications novel EMI shielding materials will be needed that provide protection against electromagnetic radiations of particular frequency range.

Mechanism of EMI Shielding

There is wide variety of EMI shielding materials used in present scenario but depending upon the mechanism of shielding, each material shows its optimum EMI shielding characteristics in certain frequency range and under certain control parameters. Generally, there are three basic mechanism of shielding reflection, absorption and multiple reflections. Reflection is a surface phenomenon and shielding through reflection mechanism required a conducting shield surface having plenty of mobile charge carriers (electrons or holes) which can interact with the electromagnetic field. Hence, electrically conducting materials are preferred although a high electrical conductivity is neither essential nor it is a scientific criterion for shielding. As metal have high electrical conductivity, they are most commonly used for EMI shielding applications where reflection of electromagnetic radiation through

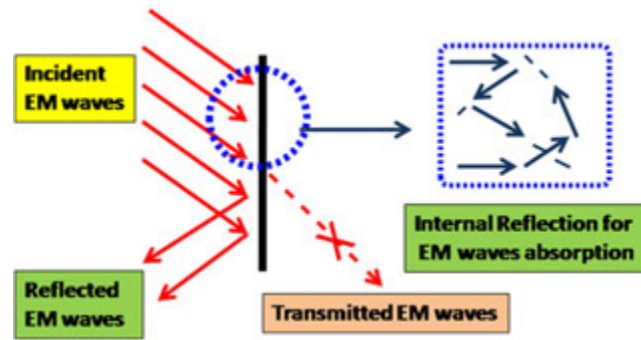


Fig. 1 Schematic representation of mechanism of EMI shielding.

the shield surface is required. Some of the metals used for shielding are copper, zinc, nickel, silver, gold, boron, tungsten, titanium or their combination materials (Tong, 2016; Azim *et al.*, 2006). Though, metals have good EMI shielding properties they suffer from corrosion, easy oxidation, low chemical resistance and poor processing methods. Moreover, metals are bulky due to high density, so metal coating is used for shielding purpose which can be made by electroplating or vacuum deposition techniques. But again it is susceptible to poor wear or scratch resistance properties.

Another important mechanism of shielding is the absorption. There are two important factors on which absorption properties of the shielding materials depends. They are the dielectric losses defined by electric permeability or dielectric constant and the magnetic losses defined by magnetic permeability. The high value of dielectric constant in a material is accountable for the generation of electric dipoles while high value of magnetic permeability is responsible for magnetic dipoles. Both electric and magnetic dipoles can interact with the electromagnetic radiations to reduce its impact (Li *et al.*, 2011; Qin and Brosseau, 2012). Based on these concepts, it is suggested that absorption mechanism required either purely dielectric materials having magnetic permeability value unity i.e., $\mu = 1$ or dominate in materials which have magnetic permeability and electric permittivity value different to one. Besides reflection and absorption, shielding can be achieved through the mechanism of multiple reflections occurs at various surfaces/interfaces present in the shielding materials. High surface area or interfacial area is the prime requirement for this mechanism. For example, porous or foam material have high surface area while composite material containing filler is an example of large interfacial area. The effect of shielding due to multiple reflections can be ignored if the distance between the reflecting surfaces/interfaces is greater than the skin depth.

Commonly, at higher frequency the electromagnetic radiations penetrate the near surface region of an electrical conducting material and electromagnetic field drops exponentially with the depth of the conducting material. This condition is called as skin effect and the depth to which fields drops to $1/e$ of the incident value is called as skin depth (Gupta *et al.*, 2013b; Zhang *et al.*, 2011). $\delta = \frac{1}{\sqrt{\pi f \mu \sigma}}$, where, f is the frequency, μ is the magnetic permeability ($\mu_0 \mu_r$), μ_0 is permeability of free space $4\pi \times 10^{-7}$ H/m, μ_r is the relative magnetic permeability and σ is the electrical conductivity in $\Omega^{-1} \text{ m}^{-1}$.

Generally, the mechanism of EMI shielding through multiple-reflections is slightly complex shown in Fig. 1. The effect of multiple-reflection is usually irrelevant in case of a highly conducting EMI shielding materials because most part of the incident electromagnetic radiations are reflected back from the conductive shield surface and limited part of electromagnetic radiations can be penetrated through the shield surface to be remains available for multiple-reflections phenomenon. On the other hand, the contribution of multiple reflections became more important in case of materials with low conductivity and high permeability. Since, electromagnetic radiations can easily penetrate inside the shielding material and most part of it is reflected and absorbed inside the surface of the shield material. The effect is more significant in low frequency while at higher frequency it reduces as the ratio between thickness of the materials and skin depth (t/δ) become larger with the increase in frequency range.

Composite Materials for Shielding

Traditional metal-based EMI shielding materials are unsuitable for advanced EMI shielding application. They are bulky and mainly work through reflection of EM radiations and cannot be used in applications where lightweight shielding materials are required like in aerospace and space structures. Furthermore, they are undesirable for applications where absorption is prime requisite. To overcome these limitations, composite materials are explored as EMI shielding materials. A composite can be a blend of two or more materials with different chemical and physical characteristics which synergized effect of each other. Therefore, it is expected that the composite system can provide better properties (physical, structural or functional) as compared to the individual constituents (Anisha *et al.*, 2018; Dhakate *et al.*, 2016). Additionally, composite materials sometimes used to redesigned one characteristic of material to overcome another characteristic. In general, composite consist of two phases i.e., continuous phase or matrix and dispersed phase or reinforcement and for composite preparation, reinforcing particles are added to the base structure i.e., matrix of another material. Since, both matrix and reinforcement phases are available in large varieties, different type of composite materials are available for EMI shielding applications. Matrix can be made of metallic, inorganic, polymeric materials and reinforcing phase can be of fibers, particles, crystals etc.

Metal matrix composites

Despite of the heavy weight problem, metals are widely used as an EMI shielding materials due to inherent advantage of high electrical conductivity (perfect ground plane for on-board electronics), EMI shielding capabilities, static charge dissipation properties etc. Therefore, researchers are paying attention to develop metal matrix composites which possess superior combination of physical/mechanical properties. As the name suggests, metal matrix composite made of matrix of metal in which reinforcement fibers or particles are uniformly embedded. Sometimes metals are also used as reinforcement in polymeric or carbon-based matrices.

Metal plate shielding theory

The capabilities of EMI shielding materials are measured in terms of shielding effectiveness (SE) value. It is defined in terms of the logarithmic ratio of incoming power (P_i) to the outgoing power (P_o) of an electromagnetic radiation falling over the materials and is expressed in decibel (dB). The shielding effectiveness values are in negative terms as outgoing power is always less than incoming power. When an EMI shielding material comes in contact with electromagnetic radiation, phenomena such as reflection, absorption and multiple reflections can be observed. Therefore, the total EMI shielding effectiveness is the sum of shielding effectiveness due to reflection (SE_R), absorption (SE_A) and multiple reflections (SE_M) and can be written mathematically in the logarithmic scale as (Gupta *et al.*, 2013b; Zhang *et al.*, 2011; Singh *et al.*, 2011b)

$$SE_T(\text{dB}) = SE_R + SE_A + SE_M = -10 \log(P_o/P_i) = -10 \log(H_o/H_i) = -10 \log(E_o/E_i) \quad (1)$$

Where, P_i & P_o are incoming power and outgoing power, H_i & H_o are the incoming and outgoing magnetic field strength and E_i & E_o are the incoming and outgoing electric field strength of electromagnetic radiation, respectively.

If the EMI shielding materials have higher shield thickness than the skin depth, the contribution of shielding effectiveness value due to multiple reflections can be neglected. In such situation, reduction in electromagnetic radiations occurs either by reflection phenomenon or absorption phenomenon and the total EMI shielding effectiveness (SE_T) can be expressed as (Gupta *et al.*, 2013a; Singh *et al.*, 2013; Ohlan *et al.*, 2008).

$$SE_T(\text{dB}) = SE_R + SE_A \quad (2)$$

Furthermore, SE_R and SE_A can be measured in terms S-parameter S_{11} (S_{22}), S_{21} (S_{12}) corresponds to reflection and the transmission coefficients, respectively;

$$T = [E_T/E_i]^2 = [S_{21}]^2 = [S_{12}]^2 \quad (3)$$

$$R = [E_R/E_i]^2 = [S_{11}]^2 = [S_{22}]^2 \quad (4)$$

The effective absorbance, A_{eff} is expressed as:

$$A_{\text{eff}} = (1 - R - T)/(1 - R) \quad (5)$$

Consequently, regarding the incident power of electromagnetic radiation falling over a shielding material, having R as the reflectance, SE due to reflectance and absorbance can be given by the expression:

$$SE_R = -10 \log_{10}(1 - R) \quad (6)$$

$$SE_A = -10 \log_{10}(1 - A_{\text{eff}}) = -10 \log_{10} \left[\frac{T}{(1 - R)} \right] \quad (7)$$

Electromagnetic radiation comprises of two fundamental components, a magnetic field (H) and an electric field (E). Both the fields are perpendicular to each other and at right angles to the plane of electromagnetic radiations containing the two components. The waveforms and its source decide the relative magnitude and ratio of E to H is defined the wave impedance. Depending upon the distance between the electromagnetic source and the shield material, electromagnetic shielding divided into near field region or far field region relative to the wavelength (λ) of the electromagnetic wave. If the distance between the electromagnetic radiation source and the shield is greater than $\lambda/2\pi$ it is called as far field shielding region whereas if this distance is less than $\lambda/2\pi$, it is the near field shielding region.

In far field shielding region, the electromagnetic waves can be considered as plane waves and both electric field (E) and magnetic field (H) are responsible for the EMI effects and satisfy the condition

$$Z = [E]/[H] \quad (8)$$

Where, Z is the wave impedance or the intrinsic impedance $[E]$ and $[H]$ are the amplitude of electric and magnetic field, respectively. For free space impedance value is always equal to 377Ω .

In case of near field shielding region, wave front is not planer but it is curved and hence, it is not parallel to the shield surface. In such situation impedance $[E]$ and $[H]$ amplitudes are not constant and depends on the distance or on the dominant field for example in an electrical radiation source, electrical field dominates over magnetic field. The intrinsic impedance is greater than 377Ω which decreases as the distance increases.

Lightweight EMI Shielding Materials

High performances EMI shielding is needed for modern electronic devices but lightweight is one of the important technical prerequisites for various EMI shielding applications especially in automobiles and aerospace industry. In lightweight EMI shielding materials polymer-based composite, aerogels and foams are attracting materials.

Polymer-Based Composites

Polymer-matrix composites possessing conductive filler has been used for EMI shielding applications because of their film forming ability which reduces or eliminates seams in the shield housing. Basically, seams are encountered in metal housing where they have a tendency of radiation leakage and consequently a diminish shielding effectiveness observed in such shield. Besides this, polymer-based composites possess low density hence suitable for lightweight shielding applications (Nimanpure *et al.*, 2018a,b). Polymer matrix is generally non conducting hence some conducting filler materials are required to improve the conductivity of the polymer matrix. Polymer-conductive filler composites can be used as a promising material for advanced EMI shielding applications such as polymers containing metallic filler or carbon based electrically conductive filler. Metallic fillers in the form of fibers or nanoparticles are dispersed in the polymer matrix to enhances the electrical conductivity of the matrix and for better interaction with the electromagnetic radiations. Injection molding is the most commonly used method for dispersion of metallic fillers in the polymer matrix (Chen *et al.*, 2008; Shyr and Shie, 2012). Drawbacks of these type of polymer composites are that the weight of the composite increases in an attempt to achieve uniform dispersion of the metallic fillers in the polymer matrix. Recently, much work has been carried out on the conducting polymers-based composites. The conductive polymer composites are advantageous because of the lightweight, low cost, film forming ability of the polymer, design flexibility, ease of processing and more importantly, the incorporation of fillers in low amount keeps the polymer being transparent to the incoming electromagnetic radiations. Most commonly used conducting polymers are polyaniline (PANI), polyacetylene, and polypyrrole etc (Lakshmi *et al.*, 2009; Singh *et al.*, 2011a). These polymers are conjugated polymers and on doping show electrical conductivity. Contrast to metallic filler which impart conductivity to the polymer matrix, molecular structure imparts electrical conductivity in case of conducting polymers. Optimization of parameters such as molecular size, polymer loading, polymer type and the synthesis process can lead to enhanced EMI shielding properties of these composites. From commercial point of view, such polymer-polymer composite framework is advantageous because lightweight being achieved with no issue of substrate flexibility as compared to those arises in the metallic or carbon-based fillers. However, these composites have some disadvantages like poor mechanical properties hence a matrix material is always required to support the structure, poor processability problem and requirement of higher filler loading for exhibiting better EMI shielding properties.

Principle points of interest of such polymer-polymer system are that the lightweight being accomplished, with no issue of substrate adaptability as those emerges in the metallic or carbon-based fillers.

Carbon based filler are extensively used to develop polymer composite for EMI shielding applications. Like metallic fillers carbon-based filler are available in various forms and aspect ratio (length to width ratio) (Nazir *et al.*, 2018; Al-Saleh *et al.*, 2013; Kim *et al.*, 2014). In general, carbon materials with high aspect ratio impart better electrical conductivity to polymer matrix. Thus, materials with high aspect ratio shows high EMI shielding effectiveness values if the filler volume fraction remains same. Whereas carbon fillers with aspect ratio are Single walled carbon nanotubes > Multiwalled carbon nanotubes > carbon nanofibers > Carbon black. Besides these fillers, using a combination of two or more types of fillers provides an efficient method to overcome the shortcomings of a single filler composites. For example, incorporation of a magnetic filler will boost the EMI shielding capability of a carbon-based EMI shielding material.

Chizari *et al.* reported the highly conductive 3D printable inks fabricated from nanocomposites of carbon nanotubes/poly(lactic acid) (CNT/PLA) with outstanding electrical conductivity up to $\sim 5000 \text{ S m}^{-1}$ (Chizari *et al.*, 2017). They used solvent-cast 3D printing to produced conductive scaffold microstructures and studied the effect of several significant basic parameters like number of layers, IFC and printing patterns on the transparency and EMI shielding effectiveness. The outcomes revealed a substantial improvement in the specific EMI SE of CNT/PLA nanocomposites printed as 3D scaffolds in contrasted with CNT/PLA hot-pressed in solid forms (~ 70 versus $\sim 37 \text{ dB g}^{-1} \text{ cm}^3$). The transparency of the frameworks could vary from $\sim 0\%$ to $\sim 75\%$ by altering their printing designs and inter-filament spacing. The reported work is highly beneficial for the manufacture and auxiliary advancement of EMI shields where light as well as transparent structures are important, for example, in aviation structures, advanced lightweight electronic gadgets or smart fabrics.

Foams and Aerogels

The specific EMI shielding effectiveness (EMI SE) is defined as total EMI SE shielding effectiveness divided by the density of the material or both density and thickness of the material. Specific EMI SE is the standard method to compare the performance of the EMI shielding materials having different density or thickness values, especially in applications where lightweight is the prime requirement. Foam structure-based composites have recently gained attention as promising EMI shielding materials due to their low density and interconnected conductive structure. The interconnected porous structure improved the shielding effectiveness through scattering or multiple reflections inside the pore walls. For example, electrically conductive fillers materials such as

Table 1 Percentage of shielding efficiency with the shielding effectiveness value according to the Eq. (1)

SE (dB)	20	30	40	50	60
Shielding efficiency (%)	99	99.9	99.99	99.999	99.9999

graphene sheets, CNTs and CNFs are used to form a conductive network structure within an insulating polymer foam matrix. Some syntactic foam like structures having hollow spheres in a matrix are also developed as lightweight EMI shielding materials. Recently, carbon foams have explored extensively for lightweight EMI shielding applications due to their low density, high surface area, interconnected conductive network and good thermal stability (Kumar *et al.*, 2013b; Zhang *et al.*, 2016). Carbon foam is a sponge like three dimensional (3D) interconnected structure of porous carbon. Earlier, carbon foams were prepared by heat treatment of thermosetting plastics in controlled conditions, later on coal tar pitch or petroleum pitches were used to prepared carbon foams. For the advanced lightweight shielding materials requirement, one dimensional (1D) CNTs or two-dimensional (2D) graphene sheets are used as filler materials into three dimensional (3D) porous structures (e.g., sponges, foams and aerogels) for achieving high EMI shielding performance with low density (Lu *et al.*, 2018; Zhang *et al.*, 2017; Wu *et al.*, 2017).

Besides foam structure, aerogel-based materials are widely explored lightweight EMI shielding applications, Aerogels as the name suggest, is a gel like porous ultralight material, in which liquid components commonly present in gel is replaced by the air. Graphene aerogels are generally used as promising EMI shielding materials (Singh *et al.*, 2015; Song *et al.*, 2015a; Liu *et al.*, 2018). A comparison of electromagnetic interference shielding effectiveness of different polymer based composite materials reported in literature are shown in Table 1.

EMI Gaskets

EMI gaskets are mechanical seams or casing that help to protect electronics devices from electromagnetic interference. EMI gaskets work by setting up a conductive path along seams and different openings in an electronic enclosure. It blocks potential difference across the shield surface to builds up a smooth current stream. Generally, gaskets plug every one of the openings in a piece of device, so that EMI radiation does not interfere with the functioning of the device. Previously, these gadgets were essentially found in radio communication and military instruments, yet because of the fast increment in EMI radiation, gaskets are normally found in the various of electronic gadgets. Mostly, gaskets must be utilized when EMI surpasses 60 dB value. Gaskets expected for EMI shielding applications are indicated to be of a construction which not only offers electrical surface conductivity even under pressure, but which also has a versatility enabling the gaskets to fit in the size of the gap between EMI shielding required structures. Additionally, the gasket materials should be durable, lightweight, economical and flexible enough to withstand repetitive compression and relaxation processes.

EMI shielding gaskets generally built as a robust core which is filled, covered or coated with an electrically conductive material. The core element typically is made of an elastomeric thermoplastic material for examples polypropylene, polyethylene, polyvinyl chloride or a thermoplastic/thermosetting rubbers such as a nitrile, chlorosulfonate, butadiene, styrene-butadiene, urethane, or silicone rubber etc., (Mottahed and Manoochehri, 1997; Shui and Chung, 1997; Zhu *et al.*, 1998; Lee, 1995). Depending upon the type of shielding required various types of gasket materials are available. Silver- or nickel-plated filler based conductive elastomers are more suited where small, precise cross sections are desired. Conductive elastomers in automated form-in-place EMI gasketing systems are also employed for enclosure parts, like wireless handset. The automated robotic system uniformly spread conductive elastomer onto metal surface or metal coated plastic housings with precise accuracy. Foam-based gaskets are used for providing shielding under low closure forces such as conductive fabric, wire mesh or metal foil over soft foam. Conductive elastomers (hollow or solid extruded) are typically used for wireless enclosure doors, panels and covers. These gaskets are more appropriate for outdoor applications as they can provide protection from both EMI and environmental risks such as moisture, corrosion etc. Knitted wire mesh type EMI gaskets, extensively used for shielding applications from so many years and now adjusted accordingly for wireless shielding design requirements. Tin-plated steel wire knitted gaskets gives a spring-like versatility when groove mounted in cast metal enclosures. The present wire mesh gaskets can divert 80% of radiations under low closure forces, permitting the utilization of more affordable enclosures area. Metal finger stock gaskets used high level of EMI shielding abilities with spring-finger wiping activity and low closure characteristics. Commonly beryllium copper (BeCu) is used for these types of gaskets. Finger stock gaskets are very flexible and impervious to pressure set. They are generally used on base station entryways where shear forces are experienced. In multiple board phones, a typical protecting approach utilizes spacer-type EMI gaskets made up of plastic and conductive elastomer. Spacer gaskets offer an EMI barrier between segments to secure against cross talk.

Different Types of Nanocomposites for EMI Shielding

Compared to conventional composites, nanocomposites are different because they contain at least one component having dimension in nanometer range (less than 100 nm) and good electrical, optical, thermal and mechanical properties. Most commonly used nanomaterials are metallic, ceramic or polymers (polyurethane, epoxy, nylon, polyepoxide, polyetherimide), ceramics

(alumina, glass, porcelain) while metals (iron, nickel, titanium) are generally used as a matrix material. As already discussed, composites contain two phases i.e., one is matrix and second is reinforcement or filler. But there is one other phase between the matrix and the filler called as interfacial phase or region which is accountable for the macroscopic properties of the nanocomposites which differ from the bulk composites. There are many challenges in the way to full exploitation of the nanocomposites such as uniform dispersion of the nanomaterials, understanding role of interfaces on bulk properties present between the different constituents, compatibility between the multiple nanomaterials. Due to their unique properties, nanocomposites are extensively investigated as potential EMI shielding materials for lightweight advanced technology.

Carbon-Based Composites and Their EMI Shielding Properties

The discoveries and research of new allotropic modifications of carbon materials have sparked considerable research interest for electromagnetic interference (EMI) shielding to address the problems of EMI pollution. As already discussed, EMI shielding works through either reflection or absorption of electromagnetic radiation, to provide protection to the instruments/electronics from the source of radiation. The versatile nature and intrinsic properties of carbon materials such as high electrical conductivity, high surface area, chemical and thermal stability have made them an efficient candidate for EMI shielding applications. Additionally, their low density is advantageous in the development of lightweight EMI shielding materials. Carbon based composite materials have been developed to improve the EMI shielding and other important properties such as flexibility, mechanical, dielectric, lifetime etc. Graphite, carbon black, carbon fibers/carbon nanofibers, carbon nanotubes, graphene/graphene oxide etc., are different carbon materials extensively used for advanced EMI shielding applications.

Graphite

Graphite has good electrical conductivity and high surface area which make them an ideal shielding material. Graphite in different forms has been reported for EMI shielding applications. Luo and Chung (Luo, 1996) first time reported the flexible graphite for EMI shielding applications. Exfoliated graphite flakes when compressed without a binder form flexible graphite sheet. Similarly, Bayer *et al.* (2012) fabricated first time the composite of colloidal graphite with Teflon for EMI shielding. Colloidal graphite is a suspension of graphite powder in a liquid medium and small amount of a polymeric binder which is conductive and can be used for EMI shielding application. Composite of expanded graphite and novolac phenolic resin (EG-NPR) is also reported for shielding application in X-band (8.2–12.4 GHz) frequency region (Gogoi and Bhattacharyya, 2014). The presence of delocalized π -electrons is responsible for the conduction network within the flakes and π -electrons accumulation at the interface of EG-NPR causes generation of electrical dipolar polarization.

Carbon fibers

Carbon fibers are very strong and lightweight strands of interconnected hexagonal carbon atoms or graphene sheets with about 5–10 μm in diameter. The excellent properties of carbon fibers such as high strength (five times higher than steel), high stiffness (2 times higher than steel), lightweight, chemical and thermal stability and low thermal expansion made them very popular as an ideal material in many industrial applications. Carbon fibers are made by the series of process involving spinning a long strand of fibers, stabilization at low temperature in presence of oxygen followed by carbonization to a very high temperature in absence of oxygen and finally treating the surface and sizing. Generally, polyacrylonitrile (PAN) is used for making turbostratic carbon fibers and mesophase pitches are used for making graphitic carbon fibers. A carbon-matrix composite containing continuous carbon fibers are recently reported as an excellent EMI shielding materials. Carbon fibers composite are the desired choice of materials over the traditional metallic alloys. Nickel and copper coated carbon fibers have been reported in this regard which shows excellent EMI shielding properties. The high electrical conductivity, high aspect ratio, ferromagnetic behavior and small diameter favors absorption of EMI radiations (Lu *et al.*, 1996; Shui and Chung, 2000). Similarly, polymer-based composites with carbon fibers as reinforcement are gaining attention because carbon fibers forms of a conductive network path within the nonconductive polymer matrix and enhances its EMI shielding ability. The conductive network depends on the fibers length and improves if the longer length fibers used. Luo and Chung (1999) compare the EMI shielding abilities of the long length continuous carbon fibers with short carbon fibers and found that former shows higher EMI shielding properties. Likewise, when short carbon fiber was compared at the same concentration with carbon black powder, higher aspect ratio of short carbon fiber provided a better shielding performance than the latter (Sau *et al.*, 1998).

Carbon black

Carbon black is one of the conductive carbon materials extensively employed for improving the conductivity of the polymer matrix. The low cost and conductive nature made it an affordable and accessible EMI shielding material. Carbon black is small carbon particle formed by thermal decomposition of hydrocarbons in the gaseous phase (Sichel, 1982). Das *et al.* (2000) reported the EMI shielding performance of carbon black and natural rubber/ethylene vinyl acetate copolymer and observed good EMI shielding properties due to voids present in the conductive framework which causes uneven variation in the reflection loss. In another study, the impact of particles contacts on conductivity and therefore the EMI shielding property was studied. Oh *et al.* developed the multilayer carbon black reinforced composites with glass and epoxy as radar absorbing materials (Oh *et al.*, 2004). Carbon black within a matrix of polypropylene has also been evaluated as an EMI shielding material by Al-Saleh and Sundararaj

(2012). They reported that uniform dispersion and distribution of the filler in the matrix play an important role in EMI shielding properties. Moreover, the parameters such as filler structure and conductivity define composite behavior, i.e., reflection or absorption.

Carbon nanotubes

The EMI shielding performance of the composites mainly depends on reinforcing material's intrinsic conductivity, aspect ratio, dielectric constant and size etc. Low density, high aspect ratio, small diameter and high electrical conductivity of carbon nanotubes have attracted interest of scientific community for developing lightweight, flexible, and electrically conductive composites with high electromagnetic interference (EMI) shielding effectiveness. High strength and/or multifunctional composites can be prepared when carbon nanotubes are used as reinforcement into metals, polymers and ceramics matrix. CNT have higher strength but lower density than carbon fibers. The high strength can be used in development of polymer/CNTs nanocomposite parts for aerospace and other high-performance applications required low loading and low density to replace commercial carbon fibers composites. In addition, CNT shows both elastic and plastic distortion behavior which can be used to relieve stresses. These properties make them soft when used in low loading but stiffer on higher loading hence can withstand large deformations without breaking. Also, it makes them an outstanding toughening nanofillers for polymer composite because this behavior is not shown by graphite fibers. Moreover, aspect ratios of CNT are higher (approximately 10,000) than other carbon fillers, thus CNT shows better electrical conductivity and mechanical properties in nanocomposite as reinforcement material (Gupta *et al.*, 2013b). The high aspect ratio and high surface area of CNTs aids in better interaction within a matrix CNTs than that of carbon fibers. Consequently, the lower CNT loading can significantly improve the mechanical strength and electrical conductivity of composites especially of polymer nanocomposite. For example, MWCNT have been used as reinforcement in polystyrene matrix and tested in the frequency range of 8.2–12.4 GHz (X band) (Yang *et al.*, 2005a). Similarly, Kim *et al.* reported the effect on electrical conductivity and EMI properties when MWCNT were used as conductive reinforcement in iron (Fe) doped poly-methyl methacrylate (PMMA) (Kim *et al.*, 2004). The presence of Fe in the composite support the electrical conductivity, charge tunneling in the composite and electromagnetic radiation absorption. Liu *et al.* prepared a layered composite of iron oxide (Fe_3O_4) and Fe incorporated MWCNT dispersed in the matrix of epoxy polymer (Liu *et al.*, 2014). Absorption dominated EMI shielding was achieved for tri-layer composite in the frequency range of 3.22–40 GHz. Similarly, core shell nanostructures ($\text{Fe}@\text{Fe}_3\text{O}_4$) decorated CNT was dispersed in a matrix of polypropylene grafted maleic anhydride (He *et al.*, 2014). Xiang *et al.* studied the EMI shielding properties of MWNT and silica composite (Xiang *et al.*, 2005). A layered composite of MWCNT in polycarbonate matrix was investigated by the Shailaja *et al.* in the X band (Pande *et al.*, 2014). Liu *et al.* reported the preparation of CNT reinforced carbon fibers/pyrolytic carbon (PyC) composites and observed that the CNT grafted in-situ made a conductive network into the pores and gaps present in the composite, thereby improving the conductivity and EMI shielding prepared CNT-C/C composites (Mei *et al.*, 2015).

Liu *et al.* reported the composite of single walled CNT dispersed in polyurethane matrix (Liu *et al.*, 2007). Huang *et al.* further continued the study by using long, short and annealed SMCNT in polymer matrix and found that in long length SWCNT the conductive network was obtained at lower loading compared to short and annealed SWCNT (Huang *et al.*, 2007). Hence, long length SWCNT shows better EMI shielding properties compared short and annealed ones. As percolation threshold for CNT is attained at very low loading. Therefore, CNT in low loading can enhance certain aspects of the composite without affecting the properties of the host matrix material and can be used for lightweight EMI shielding application especially in military and aerospace industries. Polymer matrix composites of CNT with polymers such as polyacrylate, Polyaniline (PANI), poly vinyl alcohol, acrylonitrile–butadiene–styrene, poly-tri-methylene-terephthalate, were also developed in an effort to achieved better EMI shielding properties.

Zhan *et al.* reported the natural rubber/carbon nanotubes (F-NR/CNTs) composite foams through facile latex mixing processes, i.e., rubber crosslinking and ScCO_2 foaming with excellent electromagnetic interference (EMI) performance (Zhan *et al.*, 2019). Due to the porous interconnected morphology, F-NR/CNTs possess low density, good electrical conductivity and high mechanical properties. The porous architecture results in multiple radiation reflections and scattering phenomena in between the cell matrix boundaries which leads to excellent specific shielding effectiveness of $312.69 \text{ dB cm}^2 \text{ g}^{-1}$ for F-NR/CNTs. Wang *et al.* reported the hierarchical composite of multiwall carbon nanotube (MWCNT)- $\text{Fe}_3\text{O}_4@\text{Ag}$ prepared from acylamine reaction between amino functionalized MWCNTs (MWCNTs-NH₂) and carboxylation of $\text{Fe}_3\text{O}_4@\text{Ag}$ ($\text{Fe}_3\text{O}_4@\text{Ag}-\text{COOH}$) nanoparticles (Wang *et al.*, 2019a). The work described the EMI SE of 35 dB with outstanding Young's modulus of 4.60 GPa (hardness = 0.26 GPa) and excellent thermal stability (183.4°C). The incorporation of $\text{Fe}_3\text{O}_4@\text{Ag}$ nanoparticles enhanced formation of conductive networks and offered more interfaces to reflect and reabsorb EM waves, results in improved EM wave's absorption.

Guo-Ming Weng and coworkers used unique combinations of nanostructured materials and polymers through spin spray layer-by-layer (SSLbL) to assemble $\text{Ti}_3\text{C}_2\text{Tx}$ MXene-carbon nanotube (CNT) composite films (Weng *et al.*, 2018). It is shown that semi-transparent LbL MXene-CNT composite films possess high flexibility and stability required for next generation EMI shielding applications. They used poly(vinyl alcohol) (PVA) and poly(sodium 4-styrene sulfonate) (PSS), as the key fillers for SSLbL films and reported high conductivity up to 130 S cm^{-1} with a high specific shielding effectiveness SSE/t of $58,187 \text{ dB cm}^2 \text{ g}^{-1}$, which is credited to both the improved absorption with the SSLbL design of the film and the brilliant electrical conductivity of the conductive fillers (i.e., MXene and CNT).

Graphene/graphene oxide

Graphene is 2D nanomaterial arranged sp² reinforced carbon molecules that are connected with each other in a hexagonal lattice structure. Among all the carbon-based nanomaterials graphene is found to have interesting properties, for example, high electrical

Table 2 A comparison of electromagnetic interference shielding effectiveness of different polymer based composite materials reported in literature

Material	Method	Filler loading	Thickness (mm)	EMI shielding (dB)	Electrical conductivity ($S\ cm^{-1}$)
PMMA/rGO nanocomposite (Sharif <i>et al.</i> , 2017)	Emulsifier-free emulsion polymerization	2.6 vol% rGO	2.9	63.2	91.2
EG/Polyamide 6 (PA6) composite (Duan <i>et al.</i> , 2018)	Mechanical mixing and hot pressing	2.27 vol% EG	2	25	0.55
Natural wood/Epoxy wood-derived carbon scaffolds (Shen and Feng, 2019)	Vacuum-assisted infiltration of epoxy into carbon scaffolds	7.0 vol% carbon	2	27.8	12.5
PDMS/rGO/SWCNT composite (Zhao <i>et al.</i> , 2018)	Solgel followed by backfilling approach	0.28 wt%	2	31	1.2
Fe ₃ O ₄ /TAGA/Epoxy nanocomposites (Huangfu <i>et al.</i> , 2019)	Thermal annealing	1.5/1.2 wt% Fe ₃ O ₄ /TAGA	3	35	27.5
PEDOT/rGO/SrFe ₁₂ O ₁₉ nanocomposites (Dalal <i>et al.</i> , 2019)	Emulsion polymerization	1:0.5:2.2	2.5	42.29	–
RGO/LDC aerogel (Zeng <i>et al.</i> , 2018)	Freeze-drying followed by carbonization	1:1	9.46	49.2	4.99

Source: *Poly(methyl methacrylate)/reduced graphene oxide = PMMA/rGO, Expanded graphite = EG, Thermally annealed graphene aerogel = TAGA, poly(3,4 ethylenedioxythiophene) = PEDOT, Lignin-derived carbon = LDC.

conductivity ($\approx 6000\ S/cm$), excellent mechanical strength ($\sim 1\ TPa$), large surface area ($2630\ m^2/g$) and high thermal conductivity ($\approx 5000\ W/m/K$). These appealing properties make it an amazing material for number of advanced applications, for example sensors, optoelectronics, energy storage, EMI shielding, biomedicine, and so on (Lee *et al.*, 2017a; Song *et al.*, 2014). EMI shielding of monolayer graphene is first time investigated by the Hong *et al.* (2012). They utilized polyethylene terephthalate (PET) film to move the monolayer graphene developed through chemical vapor deposition technique to study EMI properties. It is observed that monolayer graphene can block 40% of the electromagnetic radiation incident on it and EMI SE value increases linearly with increase in no. of graphene layers. The outcomes also demonstrate that monolayer graphene shows far more superior shielding performance than gold film of 10 nm thickness. Plane-wave hypothesis for metal shield is also applicable to graphene. Zhang *et al.* and Song *et al.* prepared graphene paper for EMI shielding (Song *et al.*, 2014; Zhang *et al.*, 2015a). The graphene paper shows high electrical conductivity of $233\text{--}680\ S\ cm^{-1}$ which is responsible for high EMI SE of the paper. The outcomes demonstrate graphene paper to be an ideal light weight and flexible material which can be utilized for aerospace applications. Yan *et al.* developed graphene-polystyrene composite for EMI shielding (Yan *et al.*, 2012). Chen's *et al.* prepared composites paper of iron oxide nanoparticles containing graphene oxide (GO) using an ordinary GO and thermally treated GO respectively (Chen *et al.*, 2015).

Kong *et al.* reported reduced GO (RGO) sheet containing clusters of $\gamma\text{-Fe}_2\text{O}_3$ colloidal nanoparticle (Kong *et al.*, 2013). The magnetic nanoparticles induced interfacial polarization and decrease in conductivity of reduced GO results in the absorption-dominant EMI shielding. Similarly, composite film of RGO/ $\gamma\text{-Fe}_2\text{O}_3$ /carbon fibers have also been reported (Singh *et al.*, 2012). In another study RGO-ferrofluid incorporated cement is used for investigating EMI shielding ability and results shows that strong polarization effect and magnetic loss properties of ferrofluid helped in achieving good shielding behavior (Singh *et al.*, 2011b). Similarly, $\gamma\text{-Fe}_2\text{O}_3$ decorated, RGO-PANI core-shell tubes structure have been used (Singh *et al.*, 2014). The high surface area, interfacial polarization, magnetic loss and defects formed during preparation of the hybrid composite contributes to the EMI shielding values. Sun *et al.* prepared laminated magnetic graphene using solvothermal method for EMI shielding studies (Sun *et al.*, 2013). Tung *et al.* developed a hybrid composite of Fe_2O_3 -decorated RGO and poly-3,4- ethylene di-oxy thiophene (PEDOT) (Tung *et al.*, 2012). Similarly, there are several reports of composites graphene/graphene oxide with epoxy, BaTiO₃ decorated GO graphene/graphene oxide with phenolic resins, polyurethane, poly-(ethylene oxide) (PEO), PMMA and so on (Singh *et al.*, 2012; Liang *et al.*, 2009; Hsiao *et al.*, 2013; Bai *et al.*, 2011; Zhang *et al.*, 2012).

Recently, Wang *et al.* introduced the concept of green EMI shielding using eco-mimetic 3D nanoarchitecture of Graphene/carbon/polyurethane (GCP) for green EMI shielding and obtained SE up to $\sim 54\ dB$ and outstanding green index (gs) of ~ 1.44 (Wang *et al.*, 2019b). Green shielding index (gs) is a new factor introduced in this study to evaluate environment friendliness. They reported that the unique 3-D structure in eco-mimetic nanoarchitecture results in stronger conduction loss. The honeycomb like surface is related to wedges, producing comparable wedge effect, leads to downward reflection of incident waves and suppressing secondary reflection. Furthermore, its porous structure causes multiple reflection and scattering phenomena which traps EM wave and its hierarchical structure gives more polarization centers, producing more dipoles that absorb electromagnetic energy.

Similarly, Zhang *et al.* reported the WS₂-rGO architecture for green EMI shielding and successfully achieved shielding efficiency (SE) over 32 dB in the frequency range of 2–18 GHz with an endearing green index (gs ≈ 1.0) (Zhang *et al.*, 2019). The effective green EMI SE is attributed to the staggered structure and natural dielectric properties of the WS₂ – rGO framework, including the supportive relaxation and conduction, multiple internal-scattering between the interface and void, and the comparable wedge impact.

Table 3 A comparison of electromagnetic interference shielding effectiveness of different composite materials reported in literature

Composites	Density (g/cm ⁻³)	Thickness (mm)	Frequency (GHz)	EMI SE (dB)	Specific EMI SE (dB cm ³ /g)
Carbon foam-MWCNT (Kumar <i>et al.</i> , 2013a)	0.54	2.75	8.2–12.4	85	163
Graphene-PMMA composites (Zhang <i>et al.</i> , 2011)	0.79	2.4	8.2–12.4	19	25
CNT-PS Composite Foam (Yang <i>et al.</i> , 2005a)	0.56	–	8.2–12.4	19	33
Polyimide-Graphene composite foam (Li <i>et al.</i> , 2015)	0.28	0.8	8.2–12.4	21	75
Fe ₃ O ₄ -Graphene paper (Song <i>et al.</i> , 2015b)	0.78	0.3	8.2–12.4	24	31
Fe ₃ O ₄ -RGO-PEI Composite foam (Shen <i>et al.</i> , 2013)	0.40	2.5	8.2–12.4	18	45
MCMB-MWCNT-Fe ₃ O ₄ composite paper (Chaudhary <i>et al.</i> , 2017)	0.5	0.48	8.2–12.4	80	160
PS-Graphene composite (Yan <i>et al.</i> , 2012)	0.45	2.5	8.2–12.4	29	65
PDMS-Graphene foam (Chen <i>et al.</i> , 2013)	0.06	1.0	8.2–12.4	20	333
MCMB-Fe ₃ O ₄ composite (Dhawan <i>et al.</i> , 2015)	1.6	2.5	8.2–12.4	75	47
MWCNT-Phenolic resin composite paper (Teotia <i>et al.</i> , 2014)	0.51	0.14	12.4–18	33	64
MCMB-MWCNT composite paper (Chaudhary <i>et al.</i> , 2016)	0.26	0.6	8.2–12.4	56	215
Flexible graphite (Luo, 1996)	1.1	3.1	1	130	118
Polyetherimide-Ni foam (Zhai <i>et al.</i> , 2014)	0.86	1.8	1	107	121
LCP-MWCNT (Yang <i>et al.</i> , 2005b)	1.3	1	1	60	46

Graphene nanoribbon and other miscellaneous forms

Graphene nanoribbons (GNR) are strips of graphene showing different behavior compared to its parent structure. The normal width of GNR is observed to be 12–20 nm in various regions while in case of unzipped CNT, ranges from 6 to 10 nm. Fujita *et al.* introduced the theoretical model of graphene ribbons in order to investigate the edge-dependent properties and nanoscale size effect in graphene structure. There are generally two types of edge states in GNR, zigzag and armchair that can be seen on the top portion of the side wall. GNR as graphene strips or unzipped CNT structure is a quasi 1D structure. The electronic structure of GNR is not the same as those of 2D graphene and depends on the edge states. GNR, formed through the longitudinal unzipping of CNT, are most appropriate fillers for nanocomposite materials due to their high surface area (Celis *et al.*, 2016). Composites of graphene nanoribbons have been developed and reported for energy storage, transistors, high strength materials and EMI shielding applications. Joshi *et al.* reported the GNR/PVA composite films by means of solvent casting technique and demonstrated its EMI SE at varying films thickness and GNR concentration of 0.75, 1.5 and 2.5 wt% in X-band. GNR/PVA composites of 2.5 wt% shows the highest EMI SE value at 0.6 mm thickness. In this way, these results proved the effectiveness of these types of composites in a paint that can be coated over the electronic gadgets so as to obtain excellent EMI shielding performance (Joshi *et al.*, 2013). Gupta *et al.* developed MnO₂ decorated GNR, for EMI shielding studies in Ku band frequencies (Gupta *et al.*, 2014). The MnO₂ decoration over GNR improves anisotropy energy, interfacial and electronic polarization. Similarly, Joshi *et al.* blended GNR/PANI/epoxy composites with thickness of 1.7 mm and 3.4 mm and the absorption dominated EMI SE was observed in the X band at 2.5–5 wt% concentrations of GNR (Joshi *et al.*, 2015). The developed composite shows its usefulness for advanced EMI shielding applications especially in aerospace industries because of high strength and excellent EMI shielding properties (Tables 2 and 3).

Besides the above-mentioned types of carbon composites, highly complex composites have been developed in order to meet demands of improved EMI shielding performances for advanced electronic devices. In this regard, Composites of SiCf/SiC have been developed with varying thicknesses of pyrolytic carbon interphase (Ding *et al.*, 2013). Kumar *et al.* prepared the composites of carbon foam decorated with MWCNT and nanosized iron particles and found that MWCNT carbon foam shows the excellent shielding performance (Kumar *et al.*, 2013a). Similarly, composites of CNT polystyrene foam (Yang *et al.*, 2005a), CNT buckypaper (Park *et al.*, 2009), sandwiched composite of carbon texture and epoxy (Kim *et al.*, 2014), silicone foam loaded with carbon nanotubes and functionalized graphene etc are some of the novel composite structures examined (Verdejo *et al.*, 2008).

Reinforcement With Conductive Fillers

Reinforcements or fillers are specific fibers, or fabrics used to modify or enhance properties of the matrix materials such as friction, wear resistance, electrical and thermal conductivity, flame resistance etc. Reinforcements or fillers changes the properties and structure of the materials to which they are added. They toughen or strengthen the metals, plastic or ceramics-based matrix. Generally, they are used to modify and enhance the physical and mechanical characteristics of the plastics for example electrical conductivity of the plastics gets improved when a conductive filler is added to it and consequently EMI shielding performance is improved. The conductive fillers are extensively reported for improving the electrical conductivity of the polymeric composites. Reinforcements may also lower the cost of the material by reducing the required matrix resin volume. The simplicity of processability and lightweight of fillers make them more appropriate as EMI shielding material in the composite. These conducting fillers composites have been designed typically on the basis of the filler concentration, electrical conductivity, aspect ratio and structure

of filler orientation. Different types of reinforcing materials most commonly used are the carbon fibers, nickel-plated carbon fibers, conductive paint spray and metallic mesh etc.

For achieving higher levels of shielding, a layer of conductive filler mainly metal is added to the material through the following approaches:

- (1) Foil bonded to the composite.
- (2) Copper mesh injection molded onto the composite.
- (3) Electroplated with a thin layer of copper over a nickel underplating.
- (4) Metal meshes.

Foil Bonded to the Composite

A thin foil of metal bridging two adjacent laminates is used to provide conductive pathway for flow electrons from one sheet to another. Metal foil primarily made of aluminum and copper. Initially, aluminum was one of the first choices due to its lightweight but the danger of galvanic erosion in contact with carbon fibers was the major concern and an isolation with ply of fiberglass added the extra weight to the structure. Additionally, if moisture enters the composite surface, corrosion of aluminum can occur. Copper eliminates the chances of galvanic reaction risk, but its high density, twice as much as aluminum, create again a problem. Furthermore, foils are less popular for EMI shielding enclosures and other precision shapes due to the problem of conforming the foil to the enclosures shape. To overcome the extra weight, researchers have investigated new multifunctional approaches, for example conductive paint spray and a low-resistance structural laminate etc.

Recently Zong *et al.* reported the solution-based system to prepared a large-area foil of hybrid TaS₂/organic superlattice TaS₂[hexylamine]_x[N-methylformamide]_y (TaS₂HA_{0.371}NMF_{0.135}) where organic molecules and TaS₂ monolayers are alternatively stack at atomic scale (Zong *et al.*, 2019). The hybrid foil fabricated shows outstanding mechanical flexibility together with high electrical conductivity of $1.2 \times 10^3 \text{ S cm}^{-1}$ and an electromagnetic shielding effectiveness value of 31 dB.

Yener *et al.* reported the Ni–NiAl₃ multilayer composites fabricated by using Ni and Al foils through reactive sintering in an open environment with an initial thickness of 250-μm (Yener *et al.*, 2016). The as prepared composite displays more than 50 dB EMI SE in wide frequency range (from a few GHz to over 18 GHz). Similarly, hybrid composites of characteristic natural fiber mats, aluminum sheets and epoxy resin, were developed through vacuum assisted resin transfer molding (VARTM) technique (Xia *et al.*, 2017). In the reported work, EMI shielding efficiency, flexibility, tensile strength and interior bonding characteristics of the hybrid composites were analyzed. Hybrid composites offered fantastic EMI shielding performance with good mechanical properties acquired from aluminum sheets and natural fiber-based composites, separately. Similarly, composites of stainless steel fiber (SSF)/CNTs (Shajari *et al.*, 2019), 3D Cu/Ag shell network composites (Lee *et al.*, 2019), composites of polyethylene filled with polyamide particles coated with silver (Krupa *et al.*, 2007), Ferro-Aluminum based sandwich composite (Ma *et al.*, 2016) etc., are also reported in the literature for their EMI shielding properties.

Copper Mesh Injection Molded Onto the Composite

Copper mesh has been customarily utilized on airframe structures for providing protection against EMI and lightning. Composite enclosure is covered by the copper mesh which can be injection molded onto a composite surface and offers phenomenal EMI protection of – 80 dB up to 25 GHz. The main challenge of using this method is the complete casing of whole complex structure of the enclosures.

Electroplated With a Thin Layer of Copper Over a Nickel Underplating

Copper is an excellent electrical conductor; hence copper plating is extensively used for shielding purpose in electromagnetic and radio frequency interference. In the electroplating process, a very thin layer of copper is deposited over the base metal using a strong electric field. A strong bond is made up by mechanically/chemically formulating the underlying surface of the composite. However, base metal such as iron required a nickel-based coating as passivated surfaces cannot be properly coated by the copper. Copper plating is a simple and really effective way of metal finish and therefore more popular among the concerned industries.

Copper has advantages such as high electrical conductivity and hence a very thin layer can show excellent shielding performances. Additionally, copper is soft and flexible and can be easily used for electrical parts where flexibility is the prime requirement. Furthermore, copper provide uniform surface coating which stick to the surface even on bending the surface and never shells out. Moreover, copper plating provide protection to the other metals from corrosion as it is less corrosive compared to other metals.

Metal Meshes

The acknowledgment of EMI shielding in the optoelectronic devices, particularly for optical windows or vaults, is yet a challenging task. High optical transparency and excellent EMI shielding performances are the two fundamental requirements that drive the advancement in transparent EMI shielding materials for various applications. Furthermore, under extreme situations, broadband

transmission range transparent EMI shielding materials with stable imaging quality are important for a wide range of civil, military and aviation applications (Hu *et al.*, 2012; Han *et al.*, 2015; Tan and Lu, 2007; Batrakov *et al.*, 2014). The development of the excellent EMI shielding material with all its desirable properties remains a tough innovative challenge. For high demands of shielding effectiveness with visual transparency in display windows, metal meshes are developed that display absolutely uniform black coloration and good damping values. Metal-meshes with submillimetre grade spacing and micron size linewidth are the ideal materials for high-performance transparent EMI shielding applications (Han *et al.*, 2016; Lu *et al.*, 2014). These structures show special optoelectronic characteristics, different from the trade-off relationship of conventional conductive EMI shielding materials. Conductivity of metal-meshes can be tuned through their thickness without influencing the transmittance. Accordingly, metal-meshes can be made on various substrates to fit optical transmission and EMI shielding prerequisites. A variety of wire meshes made of copper or bronze are developed for shielding electromagnetic radiations in rooms and non-optical structures. Besides this, copper, nickel and stainless steel (ferritic stainless steel) wire mesh with other composites materials are most commonly used for EMI shielding applications. Recently hybrid shielding materials composed of metal mesh or metal wires and graphene have shown tremendous potential because of their optoelectronic properties (Zhu *et al.*, 2011; Kholmanov *et al.*, 2012; Lee *et al.*, 2013; Gao *et al.*, 2015; An *et al.*, 2014; Dong *et al.*, 2014). In this regards, single-layer graphene has showed perfect shield for metals from mechanical or chemical damages (Das *et al.*, 2015; Kim *et al.*, 2016). Interestingly, the hybrid film containing highly conductive metallic mesh and monolayer graphene exhibited slight enhancement in conductivity compared to the corresponding metallic mesh only (Han *et al.*, 2017). The dominant shielding mechanism of the monolayer graphene is absorption, while that of metal meshes is reflection. Consequently, the hybrid film would be more efficient in its EMI shielding performance, due to the improvement in both reflection and absorption caused by the conductivity enhancement brought by the graphene.

EMI Characterization Methods

To measure the EMI shielding of materials, technically correct testing methods have to be developed and applied in the correct ways to ensure accurate calculations of the shielding effectiveness value. There are four different ways to calculate the EMI shielding effectiveness of a given shielding material:

- (1) Open Field or Free Space Method.
- (2) Shielded Box Method.
- (3) Shielded Room Method.
- (4) Coaxial Transmission Line Method.

Open Field Method

The open field or free space method is a technique used to estimate the shielding effectiveness of a complete electronic setup and can measure the radiations that escape from a complete assembly (Wilson *et al.*, 1988). Although, this method is unable to measure the performance of individual material but can be subject to wide frequency measurements around tens of GHz upper frequency limit. Moreover, shielding effectiveness of large size samples can be possible. Additionally, in-situ measurements are also possible and hence this test is a type of service performance for the design of complete electronic assembly.

The free space method uses certain frequency transmitting antenna for measurement depending on the required type of data (reflection or transmission values). The free space method involves placing the device at a 30 m distance from a receiving antenna and recording the electromagnetic radiation or conducted emissions transmitted down the power line. The main problems of these techniques are those associated with separation of the desired electric field from disturbing fields.

Shielded Box Method

This method is applicable for comparative measurements of samples of varying shield materials. The setup consists of a metal box and an electrically tight seam with a sample port in one wall and a receiving antenna. Also, a transmitting antenna is fitted outside the box. The antenna received the signal and its intensity is recorded by the open port and with a test specimen fitted over the port. The main disadvantages of this method are to maintain a suitable electrical contact among the shielded box and test specimens. The other problem is limited frequency range (500 MHz).

Shielded Room Method

The method is the most accurate method and has been established to overcome the limitations of shielded box method. Although, general working principle of method is the same as the shielded box method but components of the measuring system are isolated in separate rooms, for examples signal generator, transmitting and receiving antennas and recorder are confined separately to eliminate the chances of unexpected interference. Additionally, the antennas are placed in anechoic chambers of room size with large size specimen up to 2.5 m² in area capacity. As compared with the shielded box method, in this method range of the frequency and reproducibility of the data is enhanced over which consistent results can be obtained.

Coaxial Transmission Line Method

The coaxial transmission line method is the most preferred method for the measurement of shielding effectiveness in the controlled medium (Sarto and Tamburrano, 2006; Hong *et al.*, 2003). The setup consists of a holder transmission line with a vector network analyzer (VNA). The test sample is placed in coaxial transmission line holder and measured the reflection coefficient (S_{11}) and transmission coefficient (S_{22}). By measuring these scattering parameters absorption and reflection contribution to the total shielding effectiveness is determined as mentioned earlier using the Eqs. (6) and (8). The S-parameters demonstrates a 2-port network response to voltage signals generated and received at each port. The major advantage of this method is that the outcomes of different laboratories are analogous. Additionally, the coaxial transmission line can resolve the data into different components namely reflected, absorbed and transmitted. Test sample are small doughnut shaped and measurements can be performed at specific frequencies by means of a modulated signal generator, crystal detector and amplifier. Standard coaxial cables can measure a dynamic range of about 80 dB.

Summary

This article is built upon a literature study with the aims to provide the reader with a basic understanding related to the topic of EMI shielding materials and suggesting their possible explanations. In addition, a general literature review of EMI shielding techniques and its theory is presented in this article. Although various techniques and significant work have been done to make various kinds of composites materials for EMI shielding, still researchers are working in this field to accomplish better capabilities containing materials for advanced EMI shielding applications. The fundamental issues on which major work focused is the composites of lightweight shielding materials such as polymers, foams and aerogels composites but composites containing carbon nanostructures reinforcement are attracting major research interest of scientific community. Generally, composites are made at lab level and tested. It is significant to deal with the synthesis mechanism which can be scaled up and can be really utilized at industrial level. Other issues such as EMI shielding range over which the materials work as shielding materials required attentions. Endeavors are expected to improve the required composites to provide EMI shielding at various frequencies. There is additionally a requirement for understanding the instrument and mechanism of shielding in case of carbon nanostructures. More efforts are required to maintain the testing conditions for better reproducibility of EMI shielding performances.

Acknowledgments

Author, Anisha Chaudhary express her thanks to DST for providing SERB-National Post-Doctoral Fellowship (Reference no. PDF/2017/002601). Author, Subhash Nimanpure would like to thanks Council of Scientific and Industrial Research (CSIR), India for financial assistance under Research Associate Fellowship scheme (File no. 31/001(0567)/19 EMR-I).

References

- Al-Saleh, M.H., Sundararaj, U., 2012. *Journal of Physics D: Applied Physics* 46 (3), 035304.
- Al-Saleh, M.H., Saadeh, W.H., Sundararaj, U., 2013. *Carbon* 60, 146–156.
- An, B.W., Hyun, B.G., Kim, S.-Y., *et al.*, 2014. *Nano letters* 14 (11), 6322–6328.
- Anisha, C., Satish, T., Rajeev, K., *et al.*, 2018. *Materials Research Express* 5 (4), 045011.
- Azim, S.S., Satheesh, A., Ramu, K., Ramu, S., Venkatachari, G., 2006. *Progress in Organic Coatings* 55 (1), 1–4.
- Bai, X., Zhai, Y., Zhang, Y., 2011. *The Journal of Physical Chemistry C* 115 (23), 11673–11677.
- Batrakov, K., Kuzhir, P., Maksimenko, S., *et al.*, 2014. *Scientific Reports* 4, 7191.
- Bayer, I., Caramia, V., Fragouli, D., *et al.*, 2012. *Journal of Materials Chemistry* 22 (5), 2057–2062.
- Belov, L.A., Smolskiy, S.M., Kochemasov, V.N., 2012. *Handbook of RF, Microwave, and Millimeter-wave Components*. Artech house.
- Celis, A., Nair, M., Taleb-Ibrahimi, A., *et al.*, 2016. *Journal of Physics D: Applied Physics* 49 (14), 143001.
- Chaudhary, A., Kumari, S., Kumar, R., *et al.*, 2016. *ACS Applied Materials & Interfaces* 8 (16), 10600–10608.
- Chaudhary, A., Kumar, R., Teotia, S., *et al.*, 2017. *Journal of Materials Chemistry C* 5 (2), 322–332.
- Che, R., Peng, L.M., Duan, X.F., Chen, Q., Liang, X., 2004. *Advanced Materials* 16 (5), 401–405.
- Chen, C.-S., Chen, W.-R., Chen, S.-C., Chien, R.-D., 2008. *International Communications in Heat and Mass Transfer* 35 (6), 744–749.
- Chen, Y., Wang, Y., Zhang, H.-B., *et al.*, 2015. *Carbon* 82, 67–76.
- Chen, Z., Xu, C., Ma, C., Ren, W., Cheng, H.M., 2013. *Advanced Materials* 25 (9), 1296–1300.
- Chizari, K., Arjmand, M., Liu, Z., Sundararaj, U., Theriault, D., 2017. *Materials Today Communications* 11, 112–118.
- Cho, H.-S., Kim, S.-S., 1999. *IEEE Transactions on Magnetics* 35 (5), 3151–3153.
- Dalal, J., Lather, S., Gupta, A., *et al.*, 2019. *Advanced Materials Technologies* 4 (7), 1900023.
- Das, N., Khastgir, D., Chaki, T., Chakraborty, A., 2000. *Composites Part A: Applied Science and Manufacturing* 31 (10), 1069–1081.
- Das, S.R., Nian, Q., Saei, M., *et al.*, 2015. *ACS Nano* 9 (11), 11121–11133.
- Dhakate, S., Chaudhary, A., Gupta, A., *et al.*, 2016. *RSC Advances* 6 (43), 36715–36722.
- Dhawan, R., Kumari, S., Kumar, R., Dhawan, S., Dhakate, S.R., 2015. *RSC Advances* 5 (54), 43279–43289.
- Ding, D., Shi, Y., Wu, Z., *et al.*, 2013. *Carbon* 60, 552–555.
- Dong, P., Zhu, Y., Zhang, J., *et al.*, 2014. *The Journal of Physical Chemistry C* 118 (45), 25863–25868.
- Duan, H., Zhu, H., Yang, Y., *et al.*, 2018. *Journal of Materials Science: Materials in Electronics* 29 (2), 1058–1064.

- Gao, T., Li, Z., Huang, P.-s., *et al.*, 2015. *ACS Nano* 9 (5), 5440–5446.
- Gogoi, J.P., Bhattacharyya, N.S., 2014. *Journal of Applied Physics* 116 (20), 204101.
- Gupta, T.K., Singh, B.P., Dhakate, S.R., Singh, V.N., Mathur, R.B., 2013a. *Journal of Materials Chemistry A* 1 (32), 9138–9149.
- Gupta, T., Singh, B., Teotia, S., *et al.*, 2013b. *Journal of Polymer Research* 20 (6), 1–7.
- Gupta, T.K., Singh, B.P., Singh, V.N., *et al.*, 2014. *Journal of Materials Chemistry A* 2 (12), 4256–4263.
- Han, J., Wang, X., Qiu, Y., Zhu, J., Hu, P., 2015. *Carbon* 87, 206–214.
- Han, Y., Lin, J., Liu, Y., *et al.*, 2016. *Scientific Reports* 6, 25601.
- Han, Y., Liu, Y., Han, L., Lin, J., Jin, P., 2017. *Carbon* 115, 34–42.
- He, Q., Yuan, T., Zhang, X., *et al.*, 2014. *The Journal of Physical Chemistry C* 118 (42), 24784–24796.
- Hong, S.K., Kim, K.Y., Kim, T.Y., *et al.*, 2012. *Nanotechnology* 23 (45), 455704.
- Hong, Y., Lee, C., Jeong, C., *et al.*, 2003. *Review of Scientific Instruments* 74 (2), 1098–1102.
- Hsiao, S.-T., Ma, C.-C.M., Tien, H.-W., *et al.*, 2013. *Carbon* 60, 57–66.
- Hu, M., Gao, J., Dong, Y., *et al.*, 2012. *Langmuir* 28 (18), 7101–7106.
- Huang, Y., Li, N., Ma, Y., *et al.*, 2007. *Carbon* 45 (8), 1614–1621.
- Huangfu, Y., Liang, C., Han, Y., *et al.*, 2019. *Composites Science and Technology* 169, 70–75.
- Joshi, A., Bajaj, A., Singh, R., *et al.*, 2013. *Nanotechnology* 24 (45), 455705.
- Joshi, A., Bajaj, A., Singh, R., *et al.*, 2015. *Composites Part B: Engineering* 69, 472–477.
- Kholmanov, I.N., Magnuson, C.W., Aliev, A.E., *et al.*, 2012. *Nano letters* 12 (11), 5679–5683.
- Kim, B.-J., Bae, K.-M., Lee, Y.S., An, K.-H., Park, S.-J., 2014. *Surface and Coatings Technology* 242, 125–131.
- Kim, H., Kim, K., Lee, C., *et al.*, 2004. *Applied Physics Letters* 84 (4), 589–591.
- Kim, S.H., Choi, W.I., Kim, K.H., *et al.*, 2016. *Scientific Reports* 6, 33074.
- Kong, L., Yin, X., Zhang, Y., *et al.*, 2013. *The Journal of Physical Chemistry C* 117 (38), 19701–19711.
- Krupa, I., Miková, G., Novák, I., *et al.*, 2007. *European Polymer Journal* 43 (6), 2401–2413.
- Kumar, G.S., Vishnupriya, D., Joshi, A., Datar, S., Patro, T.U., 2015. *Physical Chemistry Chemical Physics* 17 (31), 20347–20360.
- Kumar, R., Dhakate, S.R., Gupta, T., *et al.*, 2013a. *Journal of Materials Chemistry A* 1 (18), 5727–5735.
- Kumar, R., Dhakate, S.R., Saini, P., Mathur, R.B., 2013b. *RSC Advances* 3 (13), 4145–4151.
- Lakshmi, K., John, H., Mathew, K., Joseph, R., George, K., 2009. *Acta Materialia* 57 (2), 371–375.
- Lee, B., 1995. *Engineering* 236 (10), 32–33.
- Lee, M.-S., Lee, K., Kim, S.-Y., *et al.*, 2013. *Nano letters* 13 (6), 2814–2821.
- Lee, S.-H., Kang, D., Oh, I.-K., 2017a. *Carbon* 111, 248–257.
- Lee, S., Yu, S., Shahzad, F., *et al.*, 2017b. *Nanoscale* 9, 13432–13440.
- Lee, S.H., Yu, S., Shahzad, F., *et al.*, 2019. *Composites Science and Technology* 182, 107778.
- Li, W.-p., Zhu, L.-q., Gu, J., Liu, H.-c., 2011. *Composites Part B: Engineering* 42 (4), 626–630.
- Li, Y., Pei, X., Shen, B., *et al.*, 2015. *RSC Advances* 5 (31), 24342–24351.
- Liang, J., Wang, Y., Huang, Y., *et al.*, 2009. *Carbon* 47 (3), 922–925.
- Liu, J., Liu, Y., Zhang, H.-B., *et al.*, 2018. *Carbon* 132, 95–103.
- Liu, Y., Song, D., Wu, C., Leng, J., 2014. *Composites Part B: Engineering* 63, 34–40.
- Liu, Z., Bai, G., Huang, Y., *et al.*, 2007. *Carbon* 45 (4), 821–827.
- Lu, D., Mo, Z., Liang, B., *et al.*, 2018. *Carbon* 133, 457–463.
- Lu, G., Li, X., Jiang, H., 1996. *Composites Science and Technology* 56 (2), 193–200.
- Lu, Z., Wang, H., Tan, J., Lin, S., 2014. *Applied Physics Letters* 105 (24), 241904.
- Luo, D.C.X., 1996. *MRS Online Proceedings Library Archive*, 445.
- Luo, X., Chung, D., 1999. *Composites Part B: Engineering* 30 (3), 227–231.
- Ma, X., Zhang, Q., Luo, Z., Lin, X., Wu, G., 2016. *Materials & Design* 89, 71–77.
- Mei, H., Wang, H., Zhang, N., *et al.*, 2015. Carbon nanotubes introduced in different phases of C/PyC/SiC composites: Effect on microstructure and properties of the materials. *Composites Science and Technology* 115.
- Mottahed, B.D., Manoochehri, S., 1997. *Polymer Engineering & Science* 37 (3), 653–666.
- Nazir, A., Yu, H., Wang, L., *et al.*, 2018. *Journal of Materials Science* 53 (12), 8699–8719.
- Nimanpure, S., Hashmi, S.A.R., Kumar, R., *et al.*, 2018a. *Polymer Composites* 39 (S4), E2175–E2184.
- Nimanpure, S., Hashmi, S.A.R., Kumar, R., Nigrawal, A., Naik, A., 2018b. *IEEE Transactions on Dielectrics and Electrical Insulation* 25 (5), 2020–2028.
- Oh, J.-H., Oh, K.-S., Kim, C.-G., Hong, C.-S., 2004. *Composites Part B: Engineering* 35 (1), 49–56.
- Ohlan, A., Singh, K., Chandra, A., Dhawan, S., 2008. *Applied Physics Letters* 93 (5), 053114–053114-3.
- Pande, S., Chaudhary, A., Patel, D., Singh, B.P., Mathur, R.B., 2014. *RSC Advances* 4 (27), 13839–13849.
- Park, J.G., Louis, J., Cheng, Q., *et al.*, 2009. *Nanotechnology* 20 (41), 415702.
- Qin, F., Brosseau, C., 2012. *Journal of Applied Physics* 111 (6), 061301.
- Sarto, M.S., Tamburrano, A., 2006. *IEEE Transactions on Electromagnetic Compatibility* 48 (2), 331–341.
- Sau, K., Chaki, T., Khastgir, D., 1998. *Polymer* 39 (25), 6461–6471.
- Shajari, S., Arjmand, M., Pawar, S.P., Sundararaj, U., Sudak, L., 2019. *Composites Part B: Engineering* 165, 662–670.
- Sharif, F., Arjmand, M., Moud, A.A., Sundararaj, U., Roberts, E.P.L., 2017. *ACS Applied Materials & Interfaces* 9 (16), 14171–14179.
- Shen, B., Zhai, W., Tao, M., Ling, J., Zheng, W., 2013. *ACS Applied Materials & Interfaces* 5 (21), 11383–11391.
- Shen, Z., Feng, J., 2019. *ACS Sustainable Chemistry & Engineering* 7 (6), 6259–6266.
- Shui, X., Chung, D., 1997. *Transactions-American Society of Mechanical Engineers Journal of Electronic Packaging* 119, 236–238.
- Shui, X., Chung, D., 2000. *Journal of Materials Science* 35 (7), 1773–1785.
- Shyr, T.-W., Shie, J.-W., 2012. *Journal of Magnetism and Magnetic Materials* 324 (23), 4127–4132.
- Sichel, E.K., 1982. *Plastics Engineering* 3.
- Singh, A.P., Chandra, A., Dhawan, S., 2011a. *AIP Advances* 1 (2), 022147.
- Singh, A.P., Mishra, M., Chandra, A., Dhawan, S., 2011b. *Nanotechnology* 22 (46), 465701.
- Singh, A.P., Garg, P., Alam, F., *et al.*, 2012. *Carbon* 50 (10), 3868–3875.
- Singh, A.P., Mishra, M., Sambyal, P., *et al.*, 2014. *Journal of Materials Chemistry A* 2 (10), 3581–3593.
- Singh, K., Ohlan, A., Pham, V.H., *et al.*, 2013. *Nanoscale* 5 (6), 2411–2420.
- Singh, S., Tripathi, P., Bhatnagar, A., *et al.*, 2015. *RSC Advances* 5 (129), 107083–107087.
- Song, Q., Ye, F., Yin, X., *et al.*, 2017. *Advanced Materials* 29, 31.
- Song, W.-L., Fan, L.-Z., Cao, M.-S., *et al.*, 2014. *Journal of Materials Chemistry C* 2 (25), 5057–5064.

- Song, W.-L., Guan, X.-T., Fan, L.-Z., *et al.*, 2015a. Carbon 93, 151–160.
- Song, W.-L., Guan, X.-T., Fan, L.-Z., *et al.*, 2015b. Journal of Materials Chemistry A 3 (5), 2097–2107.
- Sun, X., He, J., Li, G., *et al.*, 2013. Journal of Materials Chemistry C 1 (4), 765–777.
- Tan, J., Lu, Z., 2007. Optics Express 15 (3), 790–796.
- Teotia, S., Singh, B.P., Elizabeth, I., *et al.*, 2014. RSC Advances 4 (63), 33168–33174.
- Thomassin, J.-M., Lou, X., Pagnoulle, C., *et al.*, 2007. The Journal of Physical Chemistry C 111 (30), 11186–11192.
- Tong, X.C., 2016. Advanced Materials and Design for Electromagnetic Interference Shielding. CRC press.
- Tung, T.T., Feller, J.F., Kim, T., *et al.*, 2012. Journal of Polymer Science Part A: Polymer Chemistry 50 (5), 927–935.
- Verdejo, R., Saiz-Arroyo, C., Carretero-Gonzalez, J., *et al.*, 2008. European Polymer Journal 44 (9), 2790–2797.
- Wang, L., Qiu, H., Liang, C., *et al.*, 2019a. Carbon 141, 506–514.
- Wang, X.-X., Shu, J.-C., Cao, W.-Q., *et al.*, 2019b. Chemical Engineering Journal 369, 1068–1077.
- Weng, G.M., Li, J., Alhabeb, M., *et al.*, 2018. Advanced Functional Materials 28 (44), 1803360.
- Wilson, P.F., Ma, M.T., Adams, J., 1988. IEEE Transactions on Electromagnetic Compatibility 30 (3), 239–250.
- Wu, Y., Wang, Z., Liu, X., *et al.*, 2017. ACS Applied Materials & Interfaces 9 (10), 9059–9069.
- Xia, C., Yu, J., Shi, S.Q., *et al.*, 2017. Composites Part B: Engineering 114, 121–127.
- Xiang, C., Pan, Y., Liu, X., *et al.*, 2005. Applied Physics Letters 87 (12), 123103.
- Yan, D.-X., Ren, P.-G., Pang, H., *et al.*, 2012. Journal of Materials Chemistry 22 (36), 18772–18774.
- Yang, H.-J., Cao, W.-Q., Zhang, D.-Q., *et al.*, 2015. ACS Applied Materials & Interfaces 7 (13), 7073–7077.
- Yang, J., Zhang, L., Zhang, T., *et al.*, 2018. Electrochemistry Communications 87, 22–26.
- Yang, Y., Gupta, M.C., Dudley, K.L., Lawrence, R.W., 2005a. Nano Letters 5 (11), 2131–2134.
- Yang, S., Lozano, K., Lomeli, A., Foltz, H.D., Jones, R., 2005b. Composites Part A: Applied Science and Manufacturing 36 (5), 691–697.
- Yener, T., Yener, S.C., Zeytin, S., 2016. Materials and Technology 50 (6), 899–902.
- Zeng, Z., Wang, C., Zhang, Y., *et al.*, 2018. ACS Applied Materials & Interfaces 10 (9), 8205–8213.
- Zhai, W., Chen, Y., Ling, J., Wen, B., Kim, Y.-W., 2014. Journal of Cellular Plastics 50 (6), 537–550.
- Zhan, Y., Oliviero, M., Wang, J., *et al.*, 2019. Nanoscale 11 (3), 1011–1020.
- Zhang, D.-Q., Liu, T.-T., Shu, J.-C., *et al.*, 2019. ACS Applied Materials & Interfaces 11 (30), 26807–26816.
- Zhang, H.-B., Yan, Q., Zheng, W.-G., He, Z., Yu, Z.-Z., 2011. ACS Applied Materials & Interfaces 3 (3), 918–924.
- Zhang, H.-B., Zheng, W.-G., Yan, Q., Jiang, Z.-G., Yu, Z.-Z., 2012. Carbon 50 (14), 5117–5125.
- Zhang, L., Alvarez, N.T., Zhang, M., *et al.*, 2015a. Carbon 82, 353–359.
- Zhang, Y., Huang, Y., Zhang, T., *et al.*, 2015b. Advanced Materials 27 (12), 2049–2053.
- Zhang, L., Liu, M., Roy, S., *et al.*, 2016. ACS Applied Materials & Interfaces 8 (11), 7422–7430.
- Zhang, L., Liu, M., Bi, S., *et al.*, 2017. Journal of Colloid and Interface Science 493, 327–333.
- Zhao, S., Yan, Y., Gao, A., *et al.*, 2018. ACS Applied Materials & Interfaces 10 (31), 26723–26732.
- Zhu, M., Qiu, Y., Tian, J., 1998. Gongneng Cailiao/Journal of Functional Materials 29 (6), 645–647.
- Zhu, Y., Sun, Z., Yan, Z., Jin, Z., Tour, J.M., 2011. ACS Nano 5 (8), 6472–6479.
- Zong, P.A., Yoo, D., Zhang, P., *et al.*, 2019. Small 16 (15), 1901901.

Corrosion Characteristics of Metal Matrix Composites

Devadas Bhat Panemangalore and Udaya Bhat K., Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar, Karnataka, India

© 2021 Elsevier Inc. All rights reserved.

Introduction to MMCs

Definition

To obtain enhanced properties than either of the individual materials, metal matrix composites (MMCs) have evolved over the past few decades with several distinct advantages. MMCs consist of an embedded reinforcing phase that can be continuous or discontinuous in a metal matrix. The development of MMCs started in the 1950 s and several new materials are synthesized in the laboratory even today targeting various custom-made, commercial applications.

Types of Composites

Depending on the requirement of mechanical, thermal, corrosion resistance properties, etc., the material selection including matrix and reinforcement is carried out. The most common matrices include aluminum (Verma *et al.*, 2015), magnesium (Lei *et al.*, 2012), iron (Wu *et al.*, 2020), copper (Jin *et al.*, 2019), titanium (Hayat *et al.*, 2019), nickel (Munday *et al.*, 2020), nickel aluminides (Talaş and Oruç, 2020), nickel-based superalloys (Chen *et al.*, 2020) and zinc (Liu *et al.*, 2020). The reinforcements can be classified based on their aspect ratio into continuous fiber (Jiao *et al.*, 2019), monofilaments (Ward *et al.*, 2002), discontinuous fiber (Behera *et al.*, 2020), whisker (Li *et al.*, 2021), particulate (Gad *et al.*, 2020) and multi-layered laminates (Mo *et al.*, 2020). MMCs can be synthesized either by powder metallurgy route (Venkatesh and Deoghare, 2020) or via casting route (Srinivasan *et al.*, 2020). Nowadays, for structural, automotive, and aerospace applications, light metal matrix composites are also gaining importance that comprises of a light (Al, Ti, Mg) metal matrix incorporated with a reinforcement that can improve the mechanical properties and wear resistance (Jayalakshmi and Gupta, 2015). For jet engine turbines, high-temperature refractory metal-intermetallic composites that can provide enhanced toughness, oxidation, and rupture behavior have become a competitive choice of material (Jackson *et al.*, 1996).

Physical and Mechanical Properties

The reinforcements play a major role in the mechanical properties such as elastic modulus and fracture toughness of the composites, some of which depend on their interaction and orientation concerning the matrix. Physical properties such as density, specific heat, thermal conductivity, and thermal expansion coefficient values depend on the intrinsic properties of the materials. Reinforcement/matrix interface plays a vital role in the development of composites with enhanced properties. The production technologies also play a major role in developing the property profiles of metal matrix composites.

Corrosion Properties

Due to the different electrochemical behavior of the matrix and reinforcement, the MMCs are prone to galvanic corrosion. Reinforcement phases can also lead to discontinuities in the protective passive film, leading to poor corrosion resistance (Pardo *et al.*, 2005). However, with careful selection of materials, processing techniques and tailoring the microstructure, it is possible to design MMCs with enhanced corrosion resistance. The electrochemical behavior and degree of corrosion also depend on the type of environment in which the material is tested and the electrochemistry of the reinforcement. Several review articles have been published in this domain. Hihara *et al.* (Hihara and Bakkar, 2016) reviewed corrosion of metal matrix composites and listed out the electrochemical effects of the interfaces, chemical degradation, secondary effects, and measuring techniques. de la Fuente reviewed corrosion of aluminum, its alloys, and composites (de la Fuente, 2020). Ali *et al.* (2019) reviewed the corrosion properties of magnesium-based composites for medical applications. Gupta *et al.* (Gupta and Meenashisundaram, 2015) provided an insight into the processing, mechanical, and corrosion characteristics of biocompatible magnesium composites, with an emphasis on the nanocomposites. Shahin *et al.* (2019) studied the corrosion and biological perspectives of Mg nanocomposites focused on orthopedic applications. Rohatgi *et al.* (2017) reviewed the aqueous corrosion of MMCs. Uhlig's Corrosion Handbook (Revie, 2011) is an invaluable resource that covers almost all the aspects of the basics of corrosion, its detection, protection, and testing of both metals and non-metals. In the next section, several types of corrosion have been discussed.

Types of Corrosion

Several types of corrosion have been identified, some of which are localized corrosion (crevice, pitting), galvanic, flow-induced, erosion-corrosion, etc. Corrosion can also occur due to processing conditions, at high temperatures, due to interphase degradation, changes in

the microstructure, and the influence of the environment. Several critical reactions taking place during corrosion that depends on processing conditions, amount of constituents, corrosive environment (electrochemistry), characteristics of metal (metallurgy), etc. together formulates the corrosion mechanism. Based on a plethora of experimental data, a set of standard guidelines published by the American Society for Testing and Materials (ASTM) can help us to understand the corrosion failure analysis of our sample.

Localized Corrosion of MMCs

Unlike general corrosion that takes place uniformly on the entire surface, localized corrosion (Frankel and Sridhar, 2008) is an accelerated attack that involves several mechanisms such as pitting (Frankel, 1998), crevice corrosion at the matrix-reinforcement interface, exfoliation, etc. The SiC influence on the pitting behavior of AA1050 was studied by Trowsdale *et al.* (Trowsdale *et al.*, 1996). They suggested that due to the insulating behavior of SiC particles, galvanic corrosion did not get induced. Larger (20 μm) SiC particles caused enhanced localized corrosion in comparison with smaller (3 μm) particles.

Feng *et al.* (1998) studied the pitting behavior of particulate SiC reinforced AA2024 MMCs and observed localized micropitting at OCPs lower than the pitting potential, E_p .

Ding *et al.* (Ding and Hihara, 2005) observed the formation of microcrevices in B_4C , SiC and Al_2O_3 reinforced 6092-T6 Al MMCs which led to the localized anodic regions transformed into cathodic.

Lv *et al.* (2020) observed localized corrosion behavior in alumina whiskers reinforced Cu MMCs. The effect of graphite and SiC on the pitting behavior of AA 6061 MMCs was studied by Denise *et al.* (Aylor and Morgan, 1985). The crevices around the interface of SiC-Al formed the preferential sites for pitting, but the penetration depth was shallow as compared to the alloy without reinforcement.

Yao *et al.* (Yao and Zhu, 1998) studied the interfacial preferential dissolution (IPD) of SiCp/Al composites in NaCl solution, which can be wrongly identified as pitting. This mode of corrosion caused enhanced dissolution at SiC clusters and cathodic protection led to the suppression of both pitting and IPD.

Pitting corrosion behavior was also observed for cast SiCp reinforced A3xxx MMCs by Pardo *et al.* (2005) along with the presence of $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ on the surface.

Kiourtsidis *et al.* (Kiourtsidis and Skolianos, 1998) studied the corrosion behavior of squeeze-cast SiC reinforced AA2024 composites in aerated NaCl solution. The dendrite cores that are depleted of copper led to pitting and galvanic coupling that took place between the intermetallic Al_2Cu and the α -phase but the galvanic corrosion between SiC and the matrix was not observed.

Xu *et al.* (2017) studied the pitting susceptibility of Ti-based metallic glass matrix composites using a potentiodynamic polarization method in 3.5 wt% NaCl solution. The composites $\text{Ti}_{62}\text{Zr}_{12}\text{V}_{13}\text{Cu}_4\text{Be}_9$ (at%), $\text{Ti}_{58}\text{Zr}_{16}\text{V}_{10}\text{Cu}_4\text{Be}_{12}$, $\text{Ti}_{46}\text{Zr}_{20}\text{V}_{12}\text{Cu}_5\text{Be}_{17}$, and $\text{Ti}_{40}\text{Zr}_{24}\text{V}_{12}\text{Cu}_5\text{Be}_{19}$ were synthesized via arc melting and subjected to corrosion testing. The passivation film collapsed at -0.16 V versus SCE and the Cl^- ion induced pitting, which can be seen in Fig. 1. Among all the composites, the one with greater Ti at% showed better corrosion resistance due to the protective oxide film that is rich in titanium and also due to the low percentage of beryllium, which is an active element.

Galvanic Couple

Galvanic couples can be formed with the matrix being an active metal and the reinforcement that can be noble. The definition of galvanic corrosion also called bimetallic corrosion is when two or more dissimilar metals that are immersed in the same electrolyte, are in electrical contact and exhibit a significant potential difference. But MMCs also undergo galvanic corrosion due to the coupling of an active metal (matrix) with a relatively inert reinforcement such as SiC (Hihara and Latanision, 1994). Reinforcement material such as SiC monofilament in a ZE41 matrix acted as an effective oxygen reduction site, thus leading to increased corrosion rate with an increase in dissolved oxygen, which was not observed in pure Mg as well as ZE41A alloy (Hihara

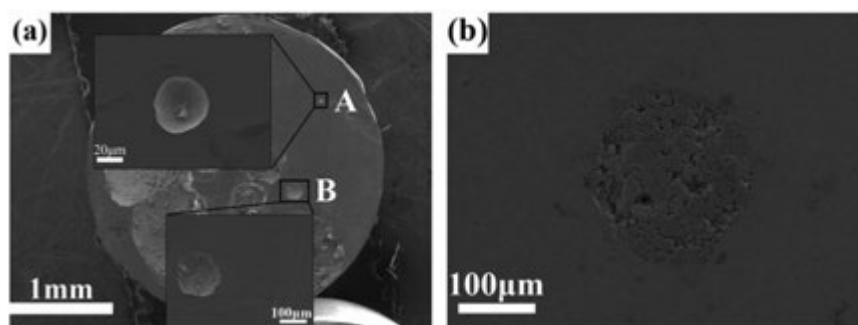


Fig. 1 SEM images at -0.16 V vs SCE before the end of the potentiodynamic polarization tests, (a) pits of $\text{Ti}_{40}\text{Zr}_{24}\text{V}_{12}\text{Cu}_5\text{Be}_{19}$ composites and (b) local corrosion region for $\text{Ti}_{46}\text{Zr}_{20}\text{V}_{12}\text{Cu}_5\text{Be}_{17}$ composites. Reproduced with permission from Xu, K.K., Lan, A.D., Yang, H.J., Han, P.D., Qiao, J. W., 2017. Corrosion behavior and pitting susceptibility of in-situ Ti-based metallic glass matrix composites in 3.5 wt% NaCl solutions. Appl. Surf. Sci. 423, 90–99. Available at: <https://doi.org/10.1016/j.apsusc.2017.06.145>.

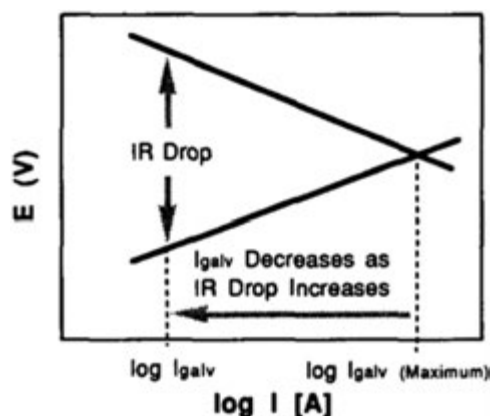


Fig. 2 Polarization diagrams depicting galvanic corrosion. Reproduced from Hihara, L.H., Latanision, R.M., 1993. Suppressing galvanic corrosion in graphite/aluminum metal-matrix composites. *Corros. Sci.* 34, 655–665. Available at: [https://doi.org/10.1016/0010-938X\(93\)90278-0](https://doi.org/10.1016/0010-938X(93)90278-0).

and Kondepudi, 1993). The corrosion rate of MMCs can also be determined by the resistivity of the ceramic reinforcement – the greater the resistivity, the minimum is the rate of corrosion (Schneider *et al.*, 2014).

Hwang *et al.* (Hwang and Kim, 2002) studied the galvanic coupling effect on the corrosion of SiC reinforced AA2214. It was found that a large cathodic polarization of the reinforcement was responsible for the lower values of the galvanic current, although the corrosion potential of the composite was higher than the alloy due to the galvanic coupling effect. Using a zero-resistance ammeter, Han *et al.* (2013) studied the galvanic corrosion of structural materials like AA6061 or SS304 with Al-B₄C composites in NaCl and H₃BO₃ solutions.

The galvanic corrosion can be studied using the polarization diagrams, as shown by Hihara *et al.* (Hihara and Latanision, 1993) via the electrical insulation method in Fig. 2. A decrease in ohmic drop between the anode and cathode of the galvanic circuit leads to an increase in the galvanic current and it is maximum with IR drop equals zero, as shown in Fig. 2. IR drop is generally calculated as the product of the resistance of the galvanic circuit times the galvanic current.

Flow Induced Corrosion

Due to the effects of turbulence in the fluid flowing over the surface of the material, the attributed corrosion effect is defined to be flow-induced (Revie, 2011). Practically it can occur at the downstream of pipe joints, orifice plates, etc. that can cause disturbed flow (Revie, 2011). Flores *et al.* (2012) studied the corrosion behavior of Ni- and Fe-based MMCs in different slurry conditions. For Ni-based MMCs, a transition from flow-induced corrosion to an erosion-corrosion process was observed.

Erosion Corrosion

The accelerated mass loss due to the combined effect of erosion and corrosion because of the relative motion between the metal and the moving corrosive fluid is erosion-corrosion, which is ubiquitous in soft metals such as aluminum. Aribo *et al.* (2017) studied the erosion-corrosion behavior of snail-shell-ash and SiC reinforced AA6063 MMC in a mono-ethylene glycol (MEG)-water environment. The erosion dominated and the material with the highest hardness was more resistant to degradation. The experiments were conducted using a submerged impinging jet rig as shown in Fig. 3. The miniature rig consisting of a single nozzle is modified from the design developed by Aribo *et al.* using a dual-nozzle arrangement. The reservoir is powered by a water pump, whose speed is controlled by altering the input voltage to the system. The aerated conditions were adapted using mono-ethylene glycol solution with NaCl and weight loss was measured after every experiment.

High-Temperature Corrosion and Oxidation

Due to the chemical reactions taking place between the material and the environment at high temperatures, severe degradation takes place. This is classified into oxidation, hot-corrosion, and sulfidation (Khanna, 2016). Elements such as aluminum, silicon, and chromium can develop adherent, stable, slow-growing, and non-permeable protective oxide scales on the surface (Li and Gao, 2008; Stott, 1992). Geng *et al.* found the improved isothermal oxidation behavior of Nb-Si-Cr-Al in-situ composites with the addition of titanium (Geng *et al.*, 2006). Bewlay *et al.* (2003) reviewed Nb-silicide-based composites for high-temperature applications above 1350°C. Additional oxidation resistance in higher-order silicide-based systems is provided by Laves phases formed by intermetallics, which also improves high-temperature creep properties. These refractory metal-intermetallic composites (RMICs) have the potential to replace Ni-based superalloys shortly.

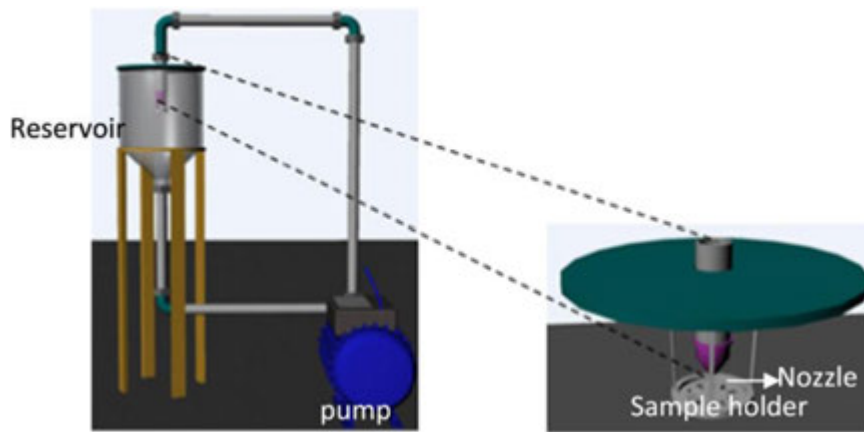


Fig. 3 Submerged Impinging Jet (SIJ) Rig. Reproduced with permission from Aribio, S., Fakorede, A., Ige, O., Olubambi, P., 2017. Erosion-corrosion behaviour of aluminum alloy 6063 hybrid composite. *Wear* 376–377, 608–614. Available at: <https://doi.org/10.1016/j.wear.2017.01.034>.

Corrosion Experiments and Sample Preparation

In the category of unpolarized-type corrosion experiments (Kirkland *et al.*, 2012), different methods include mass loss, H_2 evolution measurement, and pH monitoring. The former two require multiple samples for testing for accuracy whereas the latter requires pH change during measurement (Kirkland *et al.*, 2012). Witte *et al.* (2007) studied the corrosion behavior of Mg-hydroxyapatite (HAp) using the immersion testing method. Although this is a quick measure of determining corrosion quantitatively, several other aspects to understand the mechanisms cannot be carried out.

Polarized-type electrochemical experiments are commonly used to study the corrosion behavior of MMCs. Bhat Panemangalore *et al.* (2019) studied the corrosion behavior of silica-reinforced magnesium composites in phosphate-buffer saline (PBS) media using potentiodynamic polarization (PDP) tests. These tests provide detail on the instantaneous corrosion rates and the same unpolished sample can be tested for multiple runs (Kirkland *et al.*, 2012). Han *et al.* studied the electrochemical behavior of aluminum reinforced with B_4C composites using electrochemical impedance spectroscopy technique (Han and Chen, 2015). Kiourtsidis *et al.* (1999) used the double cyclic polarization (DCP) method to study the pitting behavior of SiCp reinforced AA2024 composites in NaCl solution. Copper depleted regions in the microstructure served as local anodes that led to greater pitting initiation sites. An increase in SiCp volume fraction did not increase the number of pits. DCP is an accelerated test and Coleman *et al.* (1990) studied the corrosion behavior of carbon/Nicalon/Saffil fiber and SiC particulate reinforcements in two different matrix metals Al-7Si and Al-4Cu in NaCl solution. For open-circuit potential tests, insulated copper wire was used to create electrical contact and epoxy resin was used to mount the specimen.

Linear Polarization Resistance Method

The linear current response generated when a material is polarized by maintaining a small voltage shift (less than 30 mV) near its corrosion potential is used to plot the current-potential curve (Ropital, 2011). The slope of this curve is polarization resistance and this test can be conducted in static/sliding conditions. Stern *et al.* (Stern and Geaby, 1957) provided a theoretical analysis of polarization plots and the polarization resistance (R_p) can be calculated by

$$R_p = \frac{B}{i_{corr}}$$

Where, $B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)}$, β_a and β_c are the Tafel coefficients and i_{corr} is the corrosion current

Electrochemical Impedance Spectroscopy Including Nyquist Plots

Electrochemical impedance spectroscopy (EIS) uses a common potentiostat to determine the frequency response of the material to an applied AC potential (Cottis, 2010; Stoynev and Vladikova, 2009). Bode and Nyquist plots can be used to understand EIS, where the former consists of a plot between impedance (Z) and phase shift (Φ) versus frequency and the latter, which is more commonly used is the plot between $-Z''$ (negative imaginary impedance) versus Z' (real part).

Microscopic Techniques

Corrosion failures can be examined using scanning electron microscopy coupled with energy-dispersive spectroscopy to identify the damage mechanisms (Pantazopoulos and Vazdirvanidis, 2014). Corrosion initiation can also be studied using an in-situ

Table 1 Corrosion rates of different metal matrix composites in varied corrosive environments

S/No	Material	Corrosive Environment	Corrosion Rate	Type of Corrosion	Reference
1	Al 6013–20SiC (temper T4)	Salt-spray	2.55 mL/y	Erosion-corrosion	(Ahmad and Abdul Aleem, 2002)
2	Al 6013–20SiC (temper F)		3.68 mL/y		
3	Al 6013–20SiC (temper O)		4.27 mL/y		
4	Al-2Mg-SiCp	3.5 wt% NaCl	0.32 mm/year	Pitting	(Candan, 2009)
5	Al-4Mg-SiCp		0.37 mm/year		
6	Al-8Mg-SiCp		0.37 mm/year		
7	Al-5Cu-20SiC	3.5 wt% NaCl	1.78 mpy		(Sivakumar <i>et al.</i> , 2018)
8	Al-5Mg-20SiC		2.69 mpy		
9	MgCa-HA/TCP composite	Hank's solution	0.176 mm/year	Galvanic corrosion	(Gu <i>et al.</i> , 2011)
10	Mg-ZnO	Simulated body fluid	0.25 mgcm ⁻² h ⁻¹	Micro-galvanic corrosion	(Lei <i>et al.</i> , 2012)
11	Mg-6SiC	1 M NaCl	18.1 mm/year		(Tiwari <i>et al.</i> , 2007)
12	Mg-16SiC		45.5 mm/year		
13	AZ92/5 vol% SiC	3.5 wt% NaCl	4.4×10^{-2} mg cm ⁻² h ⁻¹	Localized corrosion	(Pardo <i>et al.</i> , 2009)
14	AZ92/10 vol% SiC		5.6×10^{-2} mg cm ⁻² h ⁻¹		
15	Cu-2.7 vol% Al ₂ O ₃	3.5 wt% NaCl	2.397 mpy	Galvanic corrosion	(Sun and Wheat, 1993)
16	Cu-0.5 wt% Ti ₃ C ₂	9 wt% NaCl solution	1.49 mpy		(Song <i>et al.</i> , 2020)
17	Cu-1 wt% Ti ₃ C ₂		1.80 mpy		
18	Cu-2 wt% Ti ₃ C ₂		2.37 mpy		
19	Cu-2 wt% TiC		1.83 mpy		

atomic force microscopy technique and electrochemical noise techniques (Li *et al.*, 2009). To understand the corrosion mechanisms with high resolution, in-situ transmission electron microscopes can provide an in-depth analysis (Song and Xie, 2018). In-situ observation of the sample subjected to corrosion under a droplet of the corrosive media on the surface can also be analyzed using an optical microscope as a function of time (Ambat *et al.*, 2000). Using in-situ long focal video microscopy and atomic force microscopy, Payan *et al.* (2001) studied the galvanic corrosion aspect of graphite fibers reinforced Al MMCs to get quantitative information, localized study, and 3D morphology.

Corrosion Aspects of Metal Matrix Composites

In this section, corrosion behavior of different metal matrix composites is discussed. Table 1 discusses the corrosion rates of MMCs with respect to their matrix counterpart and the type of corrosion exhibited.

Processing Related Corrosion Problems and Remedies

Paciej *et al.* (Paciej and Agarwala, 1988) studied the influence of processing variables involved in heat treatment and extrusion for a SiCp reinforced AA7091 synthesized using powder metallurgy route. Enhanced corrosion resistance was observed for materials that were processed using a combined effect of modified solution heat treatment and greater extrusion ratio.

Ahmad *et al.* (Ahmad and Abdul Aleem, 1996) implemented numerous age hardening processes to study the corrosion behavior of SiC reinforced Al 6013 MMC. Naturally age-hardened (T4) exhibited enhanced corrosion resistance in comparison with annealed and as-fabricated samples due to the precipitates that are finely and homogeneously distributed in the matrix.

Yue *et al.* (1999) adapted a surface treatment using Nd: YAG laser to enhance the corrosion resistance of SiCp reinforced AA6013 MMC. Resistance to pitting was enhanced and it was attributed to the refinement and removal of Mg₂Si precipitates in the surface. They also enhanced the corrosion resistance of Mg-ZK60/SiC and Al-SiC MMCs using excimer lasers (Yue *et al.*, 1997; Zhang *et al.*, 1996). Yue *et al.* (2002) subjected the SiC reinforced AA2009 composite to different machining conditions and found that the surface finish affects the corrosion behavior. Cemented carbide turning operation exhibited lowest pitting corrosion resistance as compared to wire-electrical discharge machining and single-point diamond turning operations.

Candan *et al.* (Candan, 2009) synthesized pressure infiltrated composites of SiCp reinforced Al-Mg alloy. The intermetallic phases produced lead to the narrowing down or create discontinuities in the matrix thereby results in enhancement of corrosion resistance.

Corrosion of Al MMCs

Graedel, 1989) has reviewed the corrosion mechanisms for aluminum when it is exposed to indoor or outdoor atmosphere, in the presence of humidity, chloride, and sulfide species. Al MMCs reinforced with SiC, and Al₂O₃ have the potential to replace cast iron in engine components in the automotive industry due to their excellent tribological characteristics (Prasad and Asthana, 2004). Al alloys and composites are susceptible to several modes of localized corrosion such as intragranular, stress corrosion cracking (SCC), and

exfoliation (de la Fuente, 2020). In aluminum, the cathodic reaction takes place only at higher current densities and the migration of ions at the oxide film/solution interface is less likely due to the greater electronic resistance of the air-formed oxide film (Pryor and Keir, 1955). Turnbull (1992) reviewed several reinforcements such as SiC, graphite, Al_2O_3 , and B in Al MMCs. Hihara studied the corrosion mechanisms of graphene in Al and SiC in Al MMC in seawater and Na_2SO_4 media (Hihara, 1989). The formation of Al_4C_3 at the interfaces that has a tendency to hydrolyze led to the deterioration of degradation resistance along with the presence of residual microstructural halides that formed during the fabrication process (Hihara, 1989). Among several methods suggested to enhance the corrosion resistance of graphene in Al MMC, cathodic inhibition was effective (Hihara, 1989). SiC and TiB_2 reinforcements led to the reduction of galvanic corrosion rates of Al (Hihara and Latanision, 1992). Similar results were obtained by Griffiths *et al.* after comparing the cathodic current densities of AA6061 and SiC (Griffiths and Turnbull, 1994).

Trzaskoma *et al.* studied the corrosion behavior of SiC reinforced Al MMCs (AA2024, AA6061, and AA5456) (Trzaskoma *et al.*, 1983) in NaCl solution in the presence and absence of dissolved O_2 . The presence of oxygen affects the general corrosion behavior more than the reinforcement and except for AA2024, the pitting susceptibilities of the wrought alloys and composites did not change significantly.

Monticelli *et al.* (1997) studied the stress corrosion cracking behavior of SiCp reinforced AA6061 composites. Various localized corrosion forms were observed and the increase in corrosion rate was attributed to the tensile stress that was detected via electrochemical noise analysis. AA6061 based composites exhibited a lower corrosion rate as compared to AA2014 based composites.

Using salt-spray tests, Ahmad *et al.* (Ahmad and Abdul Aleem, 2002) studied the corrosion behavior of SiC reinforced AA 6013 MMCs and observed the formation of homogeneous protective film boehmite ($\text{AlO} \cdot \text{OH}$) contributing to the reduced corrosion rate at 100°C as compared to 50°C .

Albiter *et al.* (2006) synthesized TiC reinforced Al MMCs via pressureless melt infiltration and studied their corrosion behavior. It was found that the addition of TiC reduced the anodic current density, whereas Cu and Ti-rich particles resulted in galvanic and pitting corrosion.

Deuis *et al.* (1997) developed Al composite coatings containing Al_2O_3 , SiC or TiC synthesized using plasma-transferred arc (PTA) surfacing process on AA5083 and studied their corrosion behavior in 3.5 wt% NaCl solution. The increased volume fraction of Al_2O_3 containing coatings resulted in a lower corrosion rate. SiC and TiC additions enhanced the corrosion rate.

Datta *et al.* (2004) studied the addition of scandium on the corrosion behavior of Al-Si-Mg-SiCp MMCs prepared by the mechanical alloying route. Intermetallic phases such as Al_3Sc and AlSiSc that did not consist of Mg led to the composite containing scandium exhibiting less anodic behavior. Composites without trace additions of Sc revealed intergranular corrosion.

The effect of Cu addition on the corrosion behavior of in-situ developed Mg_2Si reinforced Al-12Si-20Mg matrix composites was studied by Palta *et al.* (2012). The addition of Cu led to form CuAl_2 phase that has a greater positive corrosion potential and led to a reduction in size and volume of Mg_2Si particles which led to an increase in corrosion resistance.

Ding *et al.* (Ding and Hihara, 2019) investigated the galvanic corrosion in B_4C reinforced AA6092 MMCs in Na_2SO_4 solution. Using the zero-resistance ammeter technique, B_4C was identified as cathodic sites that induced galvanic corrosion.

Wielage *et al.* (Wielage and Dörner, 1999) studied the corrosion studies on carbon fibers reinforced Al MMCs, where the reinforcement involved suitable corrosion protection of a pyrolytic carbon or nickel fiber coating. But the coatings did not lead to a significant enhancement in corrosion resistance.

Corrosion of Mg MMCs

Similar to Al MMCs, SiC reinforced Mg MMC also corroded uniformly without micro galvanic corrosion (Nunez-Lopez *et al.*, 1996). The addition of SiC to a ZC71 alloy matrix was studied for its corrosion behavior by Nunez-Lopez *et al.* (Lopez *et al.*, 1995). General corrosion behavior was observed by the composite tested in saline environments, using salt-spray and various electrochemical measurements.

Galvanic corrosion of SiC monofilament coupled to pure Mg and ZE41A was studied by Hihara *et al.* (Hihara and Kondepudi, 1994). Solution oxygenation led to corrosion damage in the galvanic mode as compared to de-aerated solutions, where both local and galvanic corrosion components were comparable.

Ghasali *et al.* (2019) studied the corrosion behavior of Mg- Al_2O_3 and Mg- Si_3N_4 MMCs synthesized using a microwave sintering process. Interfacial reactions led to the inhibition of corrosion and the polarization resistance exhibited was greater than that of pure Mg.

Lei *et al.* (2012) sintered the ball-milled Mg and ZnO powder mixture and obtained in-situ reinforcement of MgO ceramics and Mg-Zn intermetallics that are uniformly distributed which enhances the corrosion resistance of the MMC.

Hydroxyapatite reinforced Mg MMCs were studied for their biodegradability by Witte *et al.* (2007) and they found uniform corrosion behavior in artificial seawater and different cell solutions.

Roseline *et al.* (Roseline and Paramasivam, 2019) used fused zirconia alumina 40 (FZA40) reinforced in AA6061 using the double stir-casting technique. Reinforcements were uniformly distributed and the heat-treated composites showed decreased corrosion current densities tested in H_2SO_4 media even up to 15% reinforcement that acted as a protective layer above the surface of the alloy.

Bakkar *et al.* (Bakkar and Neubert, 2007) studied the role of alumina as a reinforcement on the corrosion resistance of Mg-based matrix. They presented a model to explain the corrosion mechanism and it is shown in Fig. 4. Exposure to oxygen leads to the formation of MgO and Al_2O_3 and it is represented in the figure as Al-containing $\text{MgO}/\text{Mg}(\text{OH})_2$ layer. This surface becomes

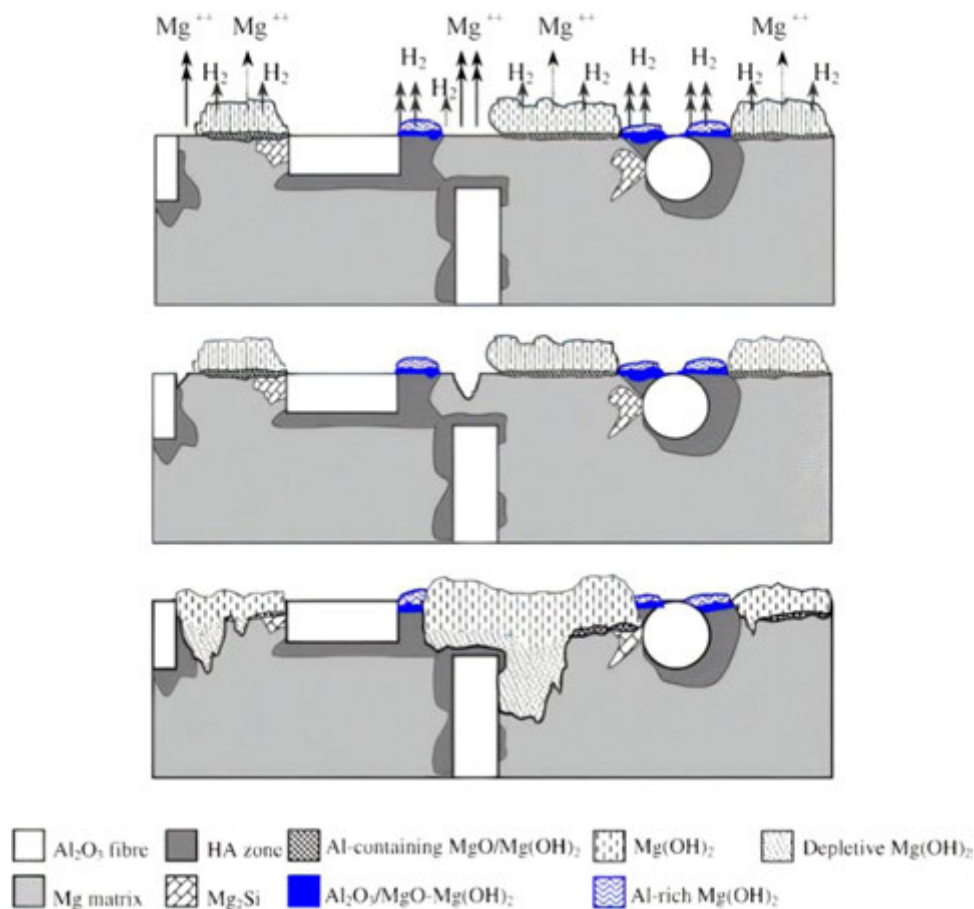


Fig. 4 A schematic representative model that shows the corrosion mechanism of alumina reinforced Mg MMC. Reproduced from Bakkar, A., Neubert, V., 2007. Corrosion characterisation of alumina-magnesium metal matrix composites. *Corros. Sci.* 49, 1110–1130. Available at: <https://doi.org/10.1016/j.corsci.2006.07.002>.

Mg(OH)_2 when reacted with an aqueous solution and with time the partially protective Al-containing MgO/Mg(OH)_2 barrier forms that wear due to Cl^- ions which then leads to pitting.

Surfaces rich in aluminum (shown as HA zone in the figure), when exposed to air, forms an initial film made of $\text{Al}_2\text{O}_3/\text{MgO-Mg(OH)}_2$ (shown blue in the figure) and an outer layer made of Al-rich Mg(OH)_2 forms. Corrosion takes place at the matrix as it is anodic compared to surfaces rich in aluminum and it forms severe pits formed via anodic reaction. This progresses with time as Mg^{2+} ions migrate outwards and Cl^- ions diffuse inwards, but the surfaces rich in aluminum are not corroded.

Bakkar *et al.* (Bakkar and Neubert, 2009) also studied the aspect of galvanic corrosion due to the carbon fiber reinforcement on Mg MMCs. Carbon fibers induce crevice corrosion at the interface that was evident in the microstructure of the sample after the polarization test in NaCl alkaline solution as seen in Fig. 5. But pitting was observed for samples subjected to free immersion condition, as seen in Fig. 6.

Falcon *et al.* (2011) studied the corrosion behavior of TiC reinforced Mg-Al composites in NaCl solution and observed that the reinforcement contributed towards resistance towards pitting.

Corrosion of Cu MMCs

Bakkar *et al.* (Bakkar and Ataya, 2014) studied the stainless steel fiber-reinforced copper metal matrix composites in chloride media. Corrosion was initiated at the copper matrix and later pitting of the reinforcement commenced. Microstructural observations post corrosion also confirmed micro galvanic corrosion mechanism.

Jin *et al.* (2019) developed a brick-and-mortar microstructure comprising graphene encapsulated copper nanoflakes as building blocks to synthesize Cu MMCs. The composite exhibited an anisotropic corrosion behavior due to the anti-corrosion effect of graphene as well as the microstructure. A schematic of the anti-corrosion role of graphene is presented as a pathway for corrosion in Fig. 7, emphasizing the role of orientation of the reinforcement in the matrix.

Wang *et al.* (2019) studied the corrosion resistance of graphene reinforced Cu MMCs prepared via powder metallurgy route. Among different compositions, 0.5 wt% graphene content had the lowest corrosion current and highest charge transfer resistance.

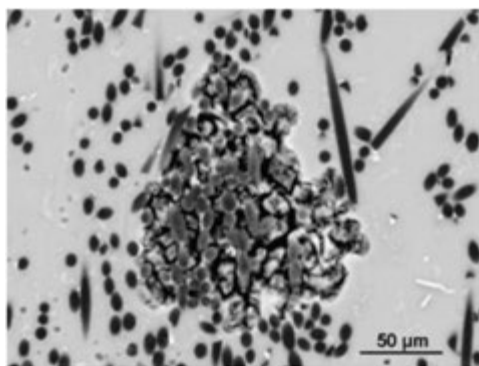


Fig. 5 SEM micrograph of carbon fiber reinforced AS41 MMC surface after polarization for 30 min at 900 mV in 100 ppm NaCl alkaline solution. Reproduced from Bakkar, A., Neubert, V., 2009. Corrosion behaviour of carbon fibres/magnesium metal matrix composite and electrochemical response of its constituents. *Electrochim. Acta* 54, 1597–1606. Available at: <https://doi.org/10.1016/j.electacta.2008.09.064>.

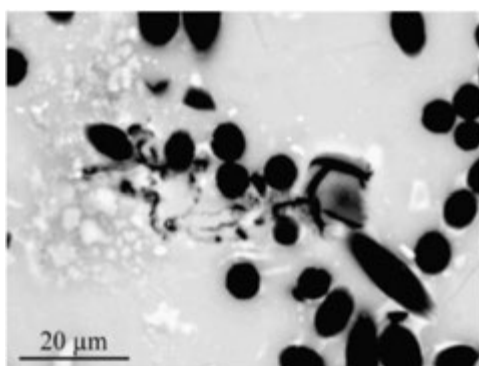


Fig. 6 SEM micrograph of the corroded surface after free immersion for 2 h at OCP condition in 100 ppm NaCl alkaline solution. Reproduced from Bakkar, A., Neubert, V., 2009. Corrosion behaviour of carbon fibres/magnesium metal matrix composite and electrochemical response of its constituents. *Electrochim. Acta* 54, 1597–1606. Available at: <https://doi.org/10.1016/j.electacta.2008.09.064>.

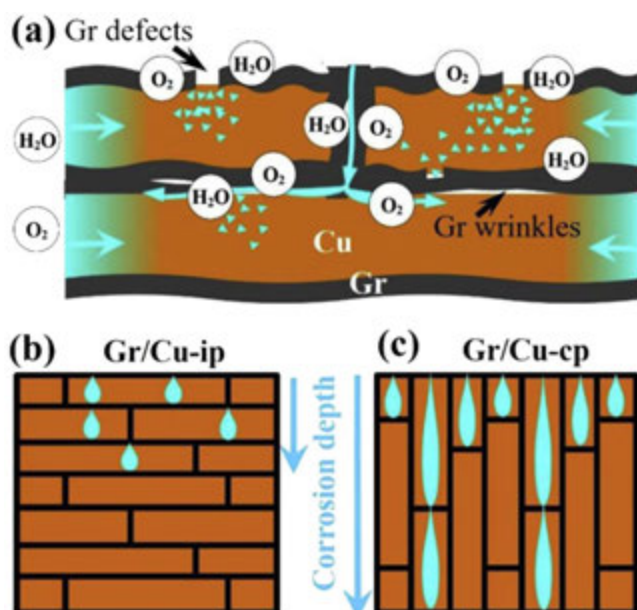


Fig. 7 (a) Schematic illustration for the possible pathway in the bulk Gr/Cu composite assembled from Cu@Gr nano-flakes. (b) Gr/Cu-in plane surface and (c) Gr/Cu-cross plane surface have different corrosion depth and rate because of graphene protection or exposed Cu matrix. Reproduced from Jin, B., Xiong, D.B., Tan, Z., *et al.*, 2019. Enhanced corrosion resistance in metal matrix composites assembled from graphene encapsulated copper nanoflakes. *Carbon* 142, 482–490. Available at: <https://doi.org/10.1016/j.carbon.2018.10.088>.

Song *et al.* (2020) studied the corrosion resistance of Ti_3C_2 reinforced Cu MMCs synthesized via spark plasma sintering technique and the Tafel plots showed the corrosion resistance of the composites greater than Cu.

Graphite and SiC reinforced hybrid Cu MMCs were synthesized by Sadhukhan *et al.* that also exhibited enhanced tribological properties (Sadhukhan and Subbarao, 2020).

Venkatesh *et al.* (Venkatesh and Rao, 2018) studied the corrosion and wear of alumina and graphite-reinforced Cu MMCs. Nano-sized alumina imparted better corrosion resistance to the Cu MMC and graphite provided the lubricating effect.

Ramesh *et al.* synthesized (Ramesh *et al.*, 2009) hybrid Cu-based composites made of a hard reinforcement SiC and soft reinforcement graphite via casting route (vortex method) targeting optimum tribological characteristics. Composites with copper-coated reinforcements also exhibited enhanced wear resistance.

Interfacial Reactions and Their Effect On Corrosion Behavior

Zhou *et al.* (2020) conducted quasi-in-situ TEM studies to understand the structural evolution of the initial stage of corrosion of the B_4C reinforced Al-Mg-Si-Cu composite. They observed the liberated Cu/Mg-rich layer from the interphase boundaries and also the redeposition of Cu clusters on $\text{Mg}(\text{Al})\text{B}_2$ nano-rods that increased the corrosion rate of the composites. A novel technique involving TEM and thermal annealing to study the interfacial reactions in MMCs was devised by Nathan *et al.* (Nathan and Ahearn, 1990).

Effect of Inhibitors

Corrosion inhibitors such as hydrazine reduce the corrosion rate of a material. They are mostly toxic chemicals and therefore there is a need to develop inhibitors that are green and sustainable (Chaubey *et al.*, 2020). Surfactants, due to their amphiphilic nature can also lead to corrosion inhibition (Zhu *et al.*, 2017). Corrosion inhibition using CeCl_3 that suppressed cathodic reactions at the interface of SiC/AA6013 was studied by Ahmad *et al.* (Ahmad and Aleem, 2009).

Conclusions

There are several aspects involved in determining the corrosion behavior of metal matrix composites, especially when there are different reinforcements, intermetallics, and their distribution, reaction with the environment, and the difference in their electrochemical potential values. The presence of stress during the working condition can also affect the corrosion properties of the composites. Crevices about the interface of matrix-reinforcement could cause pits and the inherent difference in their electrochemical behavior causes galvanic corrosion, therefore some composites also exhibit multiple corrosion mechanisms. But corrosion control can be achieved by optimum material selection and processing conditions to adapt to the working environment. Tailoring the microstructure along with understanding the reaction between its constituents helps to improve the corrosion resistance of the composite and enhance its overall performance.

References

- Ahmad, Z., Abdul Aleem, B.J., 1996. Effect of temper on seawater corrosion of an aluminum-silicon carbide composite alloy. *Corrosion* 52, 857–864. <https://doi.org/10.5006/1.3292078>.
- Ahmad, Z., Abdul Aleem, B.J., 2002. Degradation of aluminum metal matrix composites in salt water and its control. *Mater. Des.* 23, 173–180. [https://doi.org/10.1016/S0261-3069\(01\)00066-8](https://doi.org/10.1016/S0261-3069(01)00066-8).
- Ahmad, Z., Aleem, B.J.A., 2009. The effect of inhibitors on the susceptibility of Al 6013/SiC interface to localized corrosion. *J. Mater. Eng. Perform.* 18, 129–136. <https://doi.org/10.1007/s11665-008-9243-3>.
- Albiter, A., Contreras, A., Salazar, M., Gonzalez-Rodriguez, J.G., 2006. Corrosion behaviour of aluminium metal matrix composites reinforced with TiC processed by pressureless melt infiltration. *J. Appl. Electrochem.* 36, 303–308. <https://doi.org/10.1007/s10800-005-9073-z>.
- Ali, M., Hussein, M.A., Al-Aqeeli, N., 2019. Magnesium-based composites and alloys for medical applications: A review of mechanical and corrosion properties. *J. Alloy. Compd.* 792, 1162–1190. <https://doi.org/10.1016/j.jallcom.2019.04.080>.
- Ambat, R., Aung, N.N., Zhou, W., 2000. Evaluation of microstructural effects on corrosion behaviour of AZ91D magnesium alloy. *Corros. Sci.* 42, 1433–1455. [https://doi.org/10.1016/S0010-938X\(99\)00143-2](https://doi.org/10.1016/S0010-938X(99)00143-2).
- Aribo, S., Fakorede, A., Ige, O., Olubambi, P., 2017. Erosion-corrosion behaviour of aluminum alloy 6063 hybrid composite. *Wear* 376–377, 608–614. <https://doi.org/10.1016/j.wear.2017.01.034>.
- Aylor, D.M., Morgan, P.J., 1985. Effect of reinforcement on the pitting behavior of aluminum-base metal matrix composites. *J. Electrochem. Soc.* 132. <https://doi.org/10.1149/1.2114101>.
- Bakkar, A., Neubert, V., 2007. Corrosion characterisation of alumina-magnesium metal matrix composites. *Corros. Sci.* 49, 1110–1130. <https://doi.org/10.1016/j.corsci.2006.07.002>.
- Bakkar, A., Neubert, V., 2009. Corrosion behaviour of carbon fibres/magnesium metal matrix composite and electrochemical response of its constituents. *Electrochim. Acta* 54, 1597–1606. <https://doi.org/10.1016/j.electacta.2008.09.064>.
- Bakkar, A., Ataya, S., 2014. Corrosion behaviour of stainless steel fibre-reinforced copper metal matrix composite with reference to electrochemical response of its constituents. *Corros. Sci.* 85, 343–351. <https://doi.org/10.1016/j.corsci.2014.04.037>.
- Behera, A., Patel, S., Priyadarshini, M., 2020. Fiber-Reinforced Metal Matrix Nanocomposites. Elsevier. pp. 147–156. <https://doi.org/10.1016/b978-0-12-819904-6.00007-4>.

- Bewlay, B.P., Jackson, M.R., Zhao, J.C., Subramanian, P.R., 2003. A review of very-high-temperature Nb-silicide-based composites. *Metall. Mater. Trans. A* 34 A, 2043–2052. <https://doi.org/10.1007/s11661-003-0269-8>.
- Bhat Panemangalore, D., Shabadi, R., Tingaud, D., Touzin, M., Ji, G., 2019. Biocompatible silica-based magnesium composites. *J. Alloy. Compd.* 772, 49–57. <https://doi.org/10.1016/j.jallcom.2018.09.060>.
- Candan, S., 2009. An investigation on corrosion behaviour of pressure infiltrated Al-Mg alloy/SiCp composites. *Corros. Sci.* 51, 1392–1398. <https://doi.org/10.1016/j.corsci.2009.03.025>.
- Chaubey, N., Savita, Qurashi, A., Chauhan, D.S., Qurashi, M.A., 2020. Frontiers and advances in green and sustainable inhibitors for corrosion applications: A critical review. *J. Mol. Liq.* 321, 114385. <https://doi.org/10.1016/j.molliq.2020.114385>.
- Chen, Z., Wei, P., Zhang, S., *et al.*, 2020. Graphene reinforced nickel-based superalloy composites fabricated by additive manufacturing. *Mater. Sci. Eng. A* 769, 138484. <https://doi.org/10.1016/j.msea.2019.138484>.
- Coleman, S., McEnaney, B., Scott, V., 1990. Corrosion studies on metal matrix composites. *Dev. Sci. Technol. Compos. Mater.* 287–292. https://doi.org/10.1007/978-94-009-0787-4_37.
- Cottis, R.A., 2010. Shreir's Corrosion. Elsevier, pp. 1341–1373. (Electrochemical methods). <https://doi.org/10.1016/B978-044452787-5.00068-8>.
- Datta, J., Datta, S., Banerjee, M.K., Bandyopadhyay, S., 2004. Beneficial effect of scandium addition on the corrosion behavior of Al-Si-Mg-SiCp metal matrix composites. *Compos. Part A Appl. Sci. Manuf.* 35, 1003–1008. <https://doi.org/10.1016/j.compositesa.2004.03.012>.
- Devis, R.L., Green, L., Subramanian, C., Yellup, J.M., 1997. Corrosion behavior of aluminum composite coatings. *Corrosion* 53, 880–890.
- Ding, H., Hihara, L.H., 2005. Localized corrosion currents and pH profile over B4C, SiC, and Al₂O₃ reinforced 6092 aluminum composites. *J. Electrochem. Soc.* 152, (B161). <https://doi.org/10.1149/1.1870873>.
- Ding, H., Hihara, L., 2019. Electrochemical behavior of boron carbide and galvanic corrosion of boron carbide reinforced 6092 aluminum composites. *ECS Trans.* 1, 103–114. <https://doi.org/10.1149/1.2215494>.
- Falcon, L.A., Bedolla, B.E., Lemus, J., *et al.*, 2011. Corrosion behavior of Mg-Al/TiC composites in NaCl solution. *Int. J. Corros.* 2011. <https://doi.org/10.1155/2011/896845>.
- Feng, Z., Lin, C., Lin, J., Luo, J., 1998. Pitting behavior of SiCp/2024 Al metal matrix composites. *J. Mater. Sci.* 33, 5637–5642. <https://doi.org/10.1023/A:1004476501524>.
- Flores, J.F., Neville, A., Kapur, N., Gnanavelu, A., 2012. Corrosion and erosion-corrosion processes of metal-matrix composites in slurry conditions. *J. Mater. Eng. Perform.* 21, 395–405. <https://doi.org/10.1007/s11665-011-9926-z>.
- Frankel, G.S., 1998. Pitting corrosion of metals: A review of the critical factors. *J. Electrochem. Soc.* 145, 2186–2198. <https://doi.org/10.1149/1.1838615>.
- Frankel, G.S., Sridhar, N., 2008. Understanding localized corrosion. *Mater. Today* 11, 38–44. [https://doi.org/10.1016/S1369-7021\(08\)70206-2](https://doi.org/10.1016/S1369-7021(08)70206-2).
- de la Fuente, D., 2020. Corrosion of aluminum, aluminum alloys, and composites. *Modul. Mater. Sci. Mater. Eng.* <https://doi.org/10.1016/B978-0-12-819726-4.00047-8>.
- Gad, S.I., Attia, M.A., Hassan, M.A., El-Shafei, A.G., 2020. A random microstructure-based model to study the effect of the shape of reinforcement particles on the damage of elastoplastic particulate metal matrix composites. *Ceram. Int.* 47, 3444–3461. <https://doi.org/10.1016/j.ceramint.2020.09.189>.
- Geng, J., Tsakirooulos, P., Shao, G., 2006. Oxidation of Nb-Si-Cr-Al in situ composites with Mo, Ti and Hf additions. *Mater. Sci. Eng. A* 441, 26–38. <https://doi.org/10.1016/j.msea.2006.08.093>.
- Ghasali, E., Bordbar-Khiabani, A., Alizadeh, M., *et al.*, 2019. Corrosion behavior and in-vitro bioactivity of porous Mg/Al₂O₃ and Mg/Si₃N₄ metal matrix composites fabricated using microwave sintering process. *Mater. Chem. Phys.* 225, 331–339. <https://doi.org/10.1016/j.matchemphys.2019.01.007>.
- Graedel, T.E., 1989. Corrosion mechanisms for aluminum exposed to the atmosphere. *J. Electrochem. Soc.* 136, 204C–212C. <https://doi.org/10.1149/1.2096869>.
- Griffiths, A., Turnbull, A., 1994. An investigation of the electrochemical polarisation behavior of 6061 aluminum metal matrix composites. *Corros. Sci.* 36, 23–35.
- Gu, X.N., Wang, X., Li, N., *et al.*, 2011. Microstructure and characteristics of the metal–ceramic composite (MgCa-HA/TCP) fabricated by liquid metal infiltration. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 99, 127–134.
- Gupta, M., Meenashisundaram, G.K., 2015. *Insight into Designing Biocompatible Magnesium Alloys and Composites: Processing, Mechanical and Corrosion Characteristics*. Springer.
- Han, Y.M., Gallant, D., Chen, X.G., 2013. Galvanic corrosion associated with Al-B4C composites/SS₃O₄ and Al-B4C composites/AA6061 couples in NaCl and H₃BO₃ solutions. *Electrochim. Acta* 94, 134–142. <https://doi.org/10.1016/j.electacta.2013.01.115>.
- Han, Y.-M., Chen, X.-G., 2015. Electrochemical behavior of Al-B4C metal matrix composites in NaCl solution. *Materials* 8, 6455–6470. <https://doi.org/10.3390/ma8095314>.
- Hayat, M.D., Singh, H., He, Z., Cao, P., 2019. Titanium metal matrix composites: An overview. *Compos. Part A Appl. Sci. Manuf.* 121, 418–438. <https://doi.org/10.1016/j.compositesa.2019.04.005>.
- Hihara, L., Kondepudi, P.K., 1994. Galvanic corrosion between SiC monofilament and magnesium in NaCl, Na₂SO₄ and NaNO₃ solutions for application to metal-matrix composites. *Corros. Sci.* 36, 1585–1595.
- Hihara, L.H., 1989. *Corrosion of Aluminum-Matrix Composites*. Massachusetts Institute of Technology.
- Hihara, L.H., Latanision, R.M., 1992. Galvanic corrosion of aluminum-matrix composites. *Corrosion* 48, 546–552.
- Hihara, L.H., Kondepudi, P.K., 1993. The galvanic corrosion of SiC monofilament/ZE41 Mg metal-matrix composite in 0.5 M NaNO₃. *Corros. Sci.* 34. [https://doi.org/10.1016/0010-938X\(93\)90014-8](https://doi.org/10.1016/0010-938X(93)90014-8).
- Hihara, L.H., Latanision, R.M., 1993. Suppressing galvanic corrosion in graphite/aluminum metal-matrix composites. *Corros. Sci.* 34, 655–665. [https://doi.org/10.1016/0010-938X\(93\)90278-0](https://doi.org/10.1016/0010-938X(93)90278-0).
- Hihara, L.H., Latanision, R.M., 1994. Corrosion of metal matrix composites. *Int. Mater. Rev.* 39, 245–264. <https://doi.org/10.1016/B978-044452787-5.00110-4>.
- Hihara, L.H., Bakkar, A., 2016. Corrosion of metal matrix composites. *Ref. Modul. Mater. Sci. Mater. Eng.* <https://doi.org/10.1016/b978-0-12-803581-8.09807-6>.
- Hwang, W.S., Kim, H.W., 2002. Galvanic coupling effect on corrosion behavior of Al alloy-matrix composites. *Met. Mater. Int.* 8, 571–575. <https://doi.org/10.1007/BF03178259>.
- Jackson, M.R., Bewlay, B.P., Rowe, R.G., Skelly, D.W., Lipsitt, H.A., 1996. High-temperature refractory metal-intermetallic composites. *JOM* 48, 39–44. <https://doi.org/10.1007/BF03221361>.
- Jayalakshmi, S., Gupta, M., 2015. *Light Metal Matrix Composites*. Cham: Springer, pp. 7–58. https://doi.org/10.1007/978-3-319-15016-1_2.
- Jiao, F., Liu, M., Jiang, F., *et al.*, 2019. Continuous carbon fiber reinforced Ti/Al₃Ti metal-intermetallic laminate (MIL) composites fabricated using ultrasonic consolidation assisted hot pressing sintering. *Mater. Sci. Eng. A* 765, 138255. <https://doi.org/10.1016/j.msea.2019.138255>.
- Jin, B., Xiong, D.B., Tan, Z., *et al.*, 2019. Enhanced corrosion resistance in metal matrix composites assembled from graphene encapsulated copper nanoflakes. *Carbon* 142, 482–490. <https://doi.org/10.1016/j.carbon.2018.10.088>.
- Khanna, A.S., 2016. Fundamentals of high temperature oxidation/corrosion. In: Khanna, A.S. (Ed.), *High Temperature Corrosion*. World Scientific, pp. 1–31. https://doi.org/10.1142/9789814675239_0001.
- Kiourtsidis, G., Skolianos, S.M., 1998. Corrosion behavior of squeeze-cast silicon carbide-2024 composites in aerated 3.5 wt% sodium chloride. *Mater. Sci. Eng. A* 248, 165–172. [https://doi.org/10.1016/S0921-5093\(98\)00494-8](https://doi.org/10.1016/S0921-5093(98)00494-8).
- Kiourtsidis, G.E., Skolianos, S.M., Pavlidou, E.G., 1999. A study on pitting behaviour of AA2024/SiC(p) composites using the double cycle polarization technique. *Corros. Sci.* 41, 1185–1203. [https://doi.org/10.1016/S0010-938X\(98\)00179-6](https://doi.org/10.1016/S0010-938X(98)00179-6).
- Kirkland, N.T., Biribilis, N., Staiger, M.P., 2012. Assessing the corrosion of biodegradable magnesium implants: A critical review of current methodologies and their limitations. *Acta Biomater.* 8, 925–936. <https://doi.org/10.1016/j.actbio.2011.11.014>.
- Lei, T., Tang, W., Cai, S.H., Feng, F.F., Li, N.F., 2012. On the corrosion behaviour of newly developed biodegradable Mg-based metal matrix composites produced by in situ reaction. *Corros. Sci.* 54, 270–277. <https://doi.org/10.1016/j.corsci.2011.09.027>.

- Li, J., Wang, F., Shi, C., *et al.*, 2021. High strength-ductility synergy of MgAlB₄ whisker reinforced aluminum matrix composites achieved by in situ synthesis. *Mater. Sci. Eng. A* 799, 140127. <https://doi.org/10.1016/j.msea.2020.140127>.
- Li, Y., Hu, R., Wang, J., Huang, Y., Lin, C.J., 2009. Corrosion initiation of stainless steel in HCl solution studied using electrochemical noise and in-situ atomic force microscope. *Electrochim. Acta* 54, 7134–7140. <https://doi.org/10.1016/j.electacta.2009.07.042>.
- Li, Z., Gao, W., 2008. Oxidation of metal matrix composites. In *Developments in High Temperature Corrosion and Protection of Materials*. Woodhead Publishing, pp. 365–397. <https://doi.org/10.1533/9781845694258.2.365>.
- Liu, Y., Wang, X., Zhu, D., *et al.*, 2020. Enhancing strength and ductility in carbon nanotubes reinforced zinc matrix composites by in-situ formation of Zn₈. *Mater. Sci. Eng. A* 803, 140512. <https://doi.org/10.1016/j.msea.2020.140512>.
- Lopez, N.C., Skeldon, P., Thompson, G., *et al.*, 1995. The corrosion behaviour of Mg alloy ZC71/SiCp metal matrix composite. *Corros. Sci.* 37, 689–708.
- Lv, L., Jiang, X., Xiao, X., *et al.*, 2020. Study on corrosion resistance of copper matrix composites reinforced by Al₂O₃ whiskers. *Mater. Res. Express* 7, 26534. <https://doi.org/10.1088/2053-1591/ab71d0>.
- Mo, T., Chen, J., Chen, Z., *et al.*, 2020. Effect of intermetallic compounds (IMCs) on the interfacial bonding strength and mechanical properties of pre-rolling diffusion ARBed Al/Ti laminated composites. *Mater. Charact.* 170, 110731. <https://doi.org/10.1016/j.matchar.2020.110731>.
- Monticelli, C., Zucchi, F., Brunoro, G., Trabaneli, G., 1997. Stress corrosion cracking behaviour of some aluminium-based metal matrix composites. *Corros. Sci.* 39, 1949–1963. [https://doi.org/10.1016/S0010-938X\(97\)00088-7](https://doi.org/10.1016/S0010-938X(97)00088-7).
- Munday, G., Hogan, J., McDonald, A., 2020. On the microstructure-dependency of mechanical properties and failure of low-pressure cold-sprayed tungsten carbide-nickel metal matrix composite coatings. *Surf. Coat. Technol.* 396, 125947. <https://doi.org/10.1016/j.surfcoat.2020.125947>.
- Nathan, M., Ahearn, J.S., 1990. Interfacial reactions in metal matrix composites studied by a novel technique. In: Ishida, H. (Ed.), *Controlled Interphases in Composite Materials*. Netherlands: Springer, pp. 77–86. https://doi.org/10.1007/978-94-011-7816-7_8.
- Nunez-Lopez, C.A., Habazaki, H., Skeldon, P., *et al.*, 1996. An investigation of microgalvanic corrosion using a model magnesium-silicon carbide metal matrix composite. *Corros. Sci.* 38, 1721–1729. [https://doi.org/10.1016/S0010-938X\(96\)00068-6](https://doi.org/10.1016/S0010-938X(96)00068-6).
- Paciej, R.C., Agarwala, V.S., 1988. Influence of processing variables on the corrosion susceptibility of metal-matrix composites. *Corrosion* 44, 680–684. <https://doi.org/10.5006/1.3584928>.
- Palta, A., Sun, Y., Ahlatci, H., 2012. Effect of copper addition on wear and corrosion behaviours of Mg₂Si particle reinforced composites. *Mater. Des.* 36, 451–458. <https://doi.org/10.1016/j.matdes.2011.11.052>.
- Pantazopoulos, G., Vazdirvanidis, A., 2014. Identification of corrosion and damage mechanisms by using scanning electron microscopy and energy-dispersive X-ray microanalysis: Contribution to failure analysis case histories. *IOP Conf. Ser. Mater. Sci. Eng.* 55, 012015. <https://doi.org/10.1088/1757-899X/55/1/012015>.
- Pardo, A., Merino, M.C., Merino, S., *et al.*, 2005. Influence of reinforcement proportion and matrix composition on pitting corrosion behaviour of cast aluminium matrix composites (A3xx.x/SiCp). *Corros. Sci.* 47, 1750–1764. <https://doi.org/10.1016/j.corsci.2004.08.010>.
- Pardo, A., Merino, S., Merino, M.C., *et al.*, 2009. Corrosion behaviour of silicon-carbide-particle reinforced AZ92 magnesium alloy. *Corros. Sci.* 51, 841–849. <https://doi.org/10.1016/j.corsci.2009.01.024>.
- Payan, S., Le Petitcorps, Y., Olive, J.M., Saadaoui, H., 2001. Experimental procedure to analyze the corrosion mechanisms at the carbon/aluminum interface in composite materials. *Compos. Part A Appl. Sci. Manuf.* 32, 585–589. [https://doi.org/10.1016/S1359-835X\(00\)00126-3](https://doi.org/10.1016/S1359-835X(00)00126-3).
- Prasad, S.V., Asthana, R., 2004. Aluminum metal-matrix composites for automotive applications: Tribological considerations. *Tribol. Lett.* 17, 445–453. <https://doi.org/10.1023/B:TRIL.0000044492.91991.f3>.
- Pryor, M., Keir, D., 1955. The nature of aluminum as a cathode. *J. Electrochem. Soc.* 102, 605–607.
- Venkatesh, R., Rao, V.S., 2018. Thermal, corrosion and wear analysis of copper based metal matrix composites reinforced with alumina and graphite. *Def. Technol.* 14, 346–355. <https://doi.org/10.1016/j.dt.2018.05.003>.
- Ramesh, C.S., Noor Ahmed, R., Mujeebu, M.A., Abdullah, M.Z., 2009. Development and performance analysis of novel cast copper-SiC-Gr hybrid composites. *Mater. Des.* 30, 1957–1965. <https://doi.org/10.1016/j.matdes.2008.09.005>.
- Revie, W.R. (Ed.), 2011. *Uhlig's Corrosion Handbook*, third ed. John Wiley & Sons, Inc. <https://doi.org/10.1002/9780470872864>.
- Rohatgi, P.K., Xiang, C., Gupta, N., 2017. Aqueous corrosion of metal matrix composites. In: Kelly, A., Zweben, C. (Eds.), *Comprehensive Composite Materials*. Elsevier, pp. 287–312. <https://doi.org/10.1016/B978-0-12-803581-8.09985-9>.
- Ropital, F., 2011. Environmental degradation in hydrocarbon fuel processing plant: Issues and mitigation. *Adv. Clean Hydrocarb. Fuel Process. Sci. Technol.* 437–462. <https://doi.org/10.1533/9780857093783.5.437>.
- Roseline, S., Paramasivam, V., 2019. Corrosion behaviour of heat treated aluminium metal matrix composites reinforced with fused zirconia alumina 40. *J. Alloy. Compd.* 799, 205–215. <https://doi.org/10.1016/j.jallcom.2019.05.185>.
- Sadhukhan, P., Subbarao, R., 2020. Study of mechanical and tribological properties of hybrid copper metal matrix composite reinforced with graphite and SiC. *Mater. Today Proc.* 39, 1801–1806. <https://doi.org/10.1016/j.matpr.2020.08.677>.
- Schneider, M., Kremmer, K., Lämmel, C., Sempf, K., Herrmann, M., 2014. Galvanic corrosion of metal/ceramic coupling. *Corros. Sci.* 80, 191–196. <https://doi.org/10.1016/j.corsci.2013.11.024>.
- Shahin, M., Munir, K., Wen, C., Li, Y., 2019. Magnesium matrix nanocomposites for orthopedic applications: A review from mechanical, corrosion, and biological perspectives. *Acta Biomater.* 96, 1–19. <https://doi.org/10.1016/j.actbio.2019.06.007>.
- Sivakumar, S., Thimmappa, S.K., Golla, B.R., 2018. Corrosion behavior of extremely hard Al-Cu/Mg-SiC light metal alloy composites. *J. Alloy. Compd.* 767, 703–711. <https://doi.org/10.1016/j.jallcom.2018.07.117>.
- Song, G., Deng, Q., Wang, B., *et al.*, 2020. Thermal and corrosion behavior of Ti₃C₂/Copper composites. *Compos. Commun.* 22, 100498. <https://doi.org/10.1016/j.coco.2020.100498>.
- Song, Z., Xie, Z.H., 2018. A literature review of in situ transmission electron microscopy technique in corrosion studies. *Micron* 112, 69–83. <https://doi.org/10.1016/j.micron.2018.04.011>.
- Srinivasan, R., Pridhar, T., Kirubakaran, R., Ramesh, A., 2020. Prediction of wear strength of squeeze cast aluminium hybrid metal matrix composites using response surface methodology. *Mater. Today Proc.* 27, 1806–1811. <https://doi.org/10.1016/j.matpr.2020.03.779>.
- Stern, M., Geaby, A.L., 1957. Electrochemical polarization: I. A theoretical analysis of the shape of polarization curves. *J. Electrochem. Soc.* 104, (56). <https://doi.org/10.1149/1.2428496>.
- Stott, F.H., 1992. Developments in understanding the mechanisms of growth of protective scales on high-temperature alloys. *Mater. Charact.* 28, 311–325. [https://doi.org/10.1016/1044-5803\(92\)90019-E](https://doi.org/10.1016/1044-5803(92)90019-E).
- Stoyanov, Z.B., Vladikova, D.E., 2009. Measurement methods – Electrochemical: Impedance spectroscopy. In: Garche, J. (Ed.), *Encyclopedia of Electrochemical Power Sources*. Elsevier, pp. 632–642. <https://doi.org/10.1016/B978-0-44452745-5.00068-X>.
- Sun, H., Wheat, H.G., 1993. Corrosion study of Al₂O₃ dispersion strengthened Cu metal matrix composites in NaCl solutions. *J. Mater. Sci.* 28, 5435–5442. <https://doi.org/10.1007/BF00367812>.
- Talaş, Ş., Oruç, G., 2020. Characterization of TiC and TiB₂ reinforced Nickel Aluminide (NiAl) based metal matrix composites cast by in situ vacuum suction arc melting. *Vacuum* 172, 109066. <https://doi.org/10.1016/j.vacuum.2019.109066>.
- Tiwari, S., Balasubramaniam, R., Gupta, M., 2007. Corrosion behavior of SiC reinforced magnesium composites. *Corros. Sci.* 49, 711–725. <https://doi.org/10.1016/j.corsci.2006.05.047>.

- Trowsdale, A.J., Noble, B., Harris, S.J., *et al.*, 1996. The influence of silicon carbide reinforcement on the pitting behaviour of aluminium. *Corros. Sci.* 38, 177–191. [https://doi.org/10.1016/0010-938X\(96\)00098-4](https://doi.org/10.1016/0010-938X(96)00098-4).
- Trzaskoma, P.P., McCafferty, E., Crowe, C.R., 1983. Corrosion behavior of SiC/Al metal matrix composites. *J. Electrochem. Soc.* 130, 1804–1809. <https://doi.org/10.1149/1.2120102>.
- Turnbull, A., 1992. Review of corrosion studies on aluminium metal matrix composites. *Br. Corros. J.* 27, 27–35. <https://doi.org/10.1179/000705992798268864>.
- Venkatesh, V.S.S., Deoghare, A.B., 2020. Fabrication and mechanical behaviour of Al-Kaoline metal matrix composite fabricated through powder metallurgy technique. *Mater. Today Proc.* 38, 3291–3296. <https://doi.org/10.1016/j.matpr.2020.10.021>.
- Verma, A.S., Sumankant, Suri, N.M., Kaushik, Y., 2015. Corrosion behavior of aluminum base particulate metal matrix composites: A review. *Mater. Today Proc.* 2, 2840–2851. <https://doi.org/10.1016/j.matpr.2015.07.299>.
- Wang, J., Guo, L.N., Lin, W.M., *et al.*, 2019. The effects of graphene content on the corrosion resistance, and electrical, thermal and mechanical properties of graphene/copper composites. *New Carbon Mater.* 34, 161–169. [https://doi.org/10.1016/S1872-5805\(19\)60009-0](https://doi.org/10.1016/S1872-5805(19)60009-0).
- Ward, Y., Young, R.J., Shatwell, R.A., 2002. Determination of residual stresses in SiC monofilament reinforced metal-matrix composites using Raman spectroscopy. *Compos. Part A Appl. Sci. Manuf.* 33, 1409–1416. [https://doi.org/10.1016/S1359-835X\(02\)00157-4](https://doi.org/10.1016/S1359-835X(02)00157-4).
- Wielage, B., Dörner, A., 1999. Corrosion studies on aluminium reinforced with uncoated and coated carbon fibres. *Compos. Sci. Technol.* 59, 1239–1245. [https://doi.org/10.1016/S0266-3538\(98\)00163-8](https://doi.org/10.1016/S0266-3538(98)00163-8).
- Witte, F., Feyerabend, F., Maier, P., *et al.*, 2007. Biodegradable magnesium–hydroxyapatite metal matrix composites. *Biomaterials* 28, 2163–2174. <https://doi.org/10.1016/j.biomaterials.2006.12.027>.
- Wu, S., Qin, Y., Fu, D., *et al.*, 2020. Preparation and mechanism of active Mo–Mn metallization on ZTA particles surface and interfacial bonding of reinforced iron matrix composite. *Ceram. Int.* 46, 15972–15981. <https://doi.org/10.1016/j.ceramint.2020.03.147>.
- Xu, K.K., Lan, A.D., Yang, H.J., Han, P.D., Qiao, J.W., 2017. Corrosion behavior and pitting susceptibility of in-situ Ti-based metallic glass matrix composites in 3.5 wt% NaCl solutions. *Appl. Surf. Sci.* 423, 90–99. <https://doi.org/10.1016/j.apsusc.2017.06.145>.
- Yao, H.Y., Zhu, R.Z., 1998. Interfacial preferential dissolution on silicon carbide particulate/aluminum composites. *Corrosion* 54, 499–503. <https://doi.org/10.5006/1.3284877>.
- Yue, T.M., Wang, A.H., Man, H.C., 1997. Improvement in the corrosion resistance of magnesium ZK60/SiC composite by excimer laser surface treatment. *Scr. Mater.* 38, 191–198. [https://doi.org/10.1016/S1359-6462\(97\)00495-8](https://doi.org/10.1016/S1359-6462(97)00495-8).
- Yue, T.M., Wu, Y.X., Man, H.C., 1999. Laser surface treatment of aluminium 6013/SiC_p composite for corrosion resistance enhancement. *Surf. Coat. Technol.* 114, 13–18. [https://doi.org/10.1016/S0257-8972\(99\)00015-8](https://doi.org/10.1016/S0257-8972(99)00015-8).
- Yue, T.M., Yu, J.K., Man, H.C., 2002. Corrosion behavior of aluminum 2009/SiC composite machined to different conditions. *J. Mater. Sci. Lett.* 21, 1069–1072. <https://doi.org/10.1023/A:1016542013042>.
- Zhang, X.M., Man, H.C., Yue, T.M., 1996. Corrosion properties of excimer laser surface treated Al–SiC metal matrix composite. *Scr. Mater.* 35, 1095–1100. [https://doi.org/10.1016/1359-6462\(96\)00265-5](https://doi.org/10.1016/1359-6462(96)00265-5).
- Zhou, Y.T., Zan, Y.N., Wang, Q.Z., *et al.*, 2020. Atomic-scale quasi in-situ TEM observation on the redistribution of alloying element Cu in a B4C/Al composite at the initial stage of corrosion. *Corros. Sci.* 174. <https://doi.org/10.1016/j.corsci.2020.108808>.
- Zhu, Y., Free, M.L., Woollam, R., Durnie, W., 2017. A review of surfactants as corrosion inhibitors and associated modeling. *Prog. Mater. Sci.* 90, 159–223. <https://doi.org/10.1016/j.pmatsci.2017.07.006>.

Coating Technologies for Metal Matrix Composites

Sumit Pramanik, Department of Mechanical Engineering, SRM Institute of Science and Technology, Kancheepuram, Tamil Nadu, India

Kamal K Kar, Department of Mechanical Engineering and Materials Science Programme, Indian Institute of Technology Kanpur, Kanpur, India

© 2021 Elsevier Inc. All rights reserved.

Glossary

Anti-icing Anti-icing surfaces are profoundly hydrophobic and are extremely difficult to wet.

Anti-oxidation It is used to protect metallic components from the oxidation attack.

Anti-soiling It is used to reduce soiling or yielding them easier to wash.

Coating It is used to provide protection and/or functional properties to the substrate's surfaces.

Composite It is a physically distinct and chemically inhomogeneous mixture of two more different phases or solids.

Corrosion It is a kind of chemical attack occurred at the surface or subsurface of solid materials.

Fog-resistance It is a resistance of the material against a small droplet of condensed water on substrate from the surrounding atmosphere.

Hydrophobicity It is a property of material's surface which repels the water molecules.

Metal matrix composite It is a physically distinct and chemically inhomogeneous mixture between two more different phases in metallic (i.e., metal or alloy) matrix.

Oleophobicity It is a property of material's surface which repels lipid or oleic molecules.

Scratch resistance It is a property of material's surface that resists the producing continuous mark, visible to the naked eye, with minimum loading.

Self-cleaning It very similar to the anti-soiling coating.

Self-healing It is a type of coatings that can autonomically repair and prevent surface attacks.

Superelectrophobicity It describes the nature of foreign atoms in a metal, i.e., known as "solvent of electrons" and it presents between the impurities having closed electron shell structure, which leads their dissolution properties in a metal.

Superhydrophobicity It is a property of material's surface composed of such water-repellent materials on that water droplets bounce such a manner that it actually seem backlash bounce off like as rubber balls.

Introduction

Recently, the coating on metal matrix composites (MMCs) is emerged as a fascinating material to the researchers in the world due to their various mechanical, thermal, electrical, biocompatible properties in several advanced applications (Pramanik *et al.*, 2017). MMCs are a kind of composite materials in which one metal or alloy must be as a form of matrix phase, which can be reinforced with at least one other reinforcing material of either any high melting point metallic material or any ceramic material. In another word, the metal matrix is a continuous kind of monolithic material into which the reinforcement is dispersed. Mainly in structural applications at low or ambient temperature, the most commonly used matrix material is a low-density metal or alloys such as magnesium (Mg), aluminum (Al), titanium (Ti), nickel (Ni), copper (Cu), or their alloys, which provides flexible support to the reinforcing agent. But in high-temperature applications, the metallic matrices based on cobalt (Co), Co-Ni alloy, and so on are commonly used. On the other hand, reinforcing particulate (i.e., particles, discontinuous fibers, whiskers, short fibers, chopped fibers, etc.) do not always deliver a purely structural function, instead provides improved physical characteristics such as tribological properties including, friction coefficient, wear resistance, thermal conductivity, thermal expansion coefficient and so on (Pramanik *et al.*, 2017). It has been found that the randomly dispersed discontinuous MMCs are isotropic in nature (Böhm *et al.*, 2002) and thus, they are easy to be worked with different conventional metalworking processes such as forging, rolling extrusion, machining, and so on (Barnes *et al.*, 1996). Further, using continuous aligned reinforcement with monofilament wires, fibers, laminate or fabrics material such as alumina (Al_2O_3) (Zhai *et al.*, 1997), silicon carbide (SiC) (Zimmerman *et al.*, 2002), and carbon fiber (CF) (Shirvanimoghaddam *et al.*, 2017), a certain directional or anisotropic structure can be developed to influence the strength of MMCs. In particular, as the specific strength, σ_{sp} (i.e., $\sigma_{sp} = \sigma_{UST}/\rho$ where σ_{UST} is ultimate tensile strength (UTS) and ρ is density) and specific modulus, E_{sp} (i.e., $E_{sp} = E/\rho$ where E is Young's modulus) are very crucial for comparing the composite's overall mechanical properties, a typical comparison of potential matrix and reinforcement materials aerospace applications is depicted in Fig. 1 (Rohatgi and Schultz, 2007; Allison and Cole, 1993).

There are significant applications of MMCs in various fields, particularly in automobile sectors (Prasad and Asthana, 2004; Rohatgi, 1991; Miracle, 2005), aeronautical (Deuis *et al.*, 1998), biomedical engineering (Witte *et al.*, 2007), sports industries, and so on (Clyne and Withers, 1995). The need for high-performance materials to acquire challenging demands is being increased tremendously in those fields. The main advantage of the MMCs in comparison with their monolithic alloys is tunable specific desired properties (Ataollahi Oshkour *et al.*, 2014). The most important desired properties of the MMCs are listed as (Moghadam *et al.*, 2014).

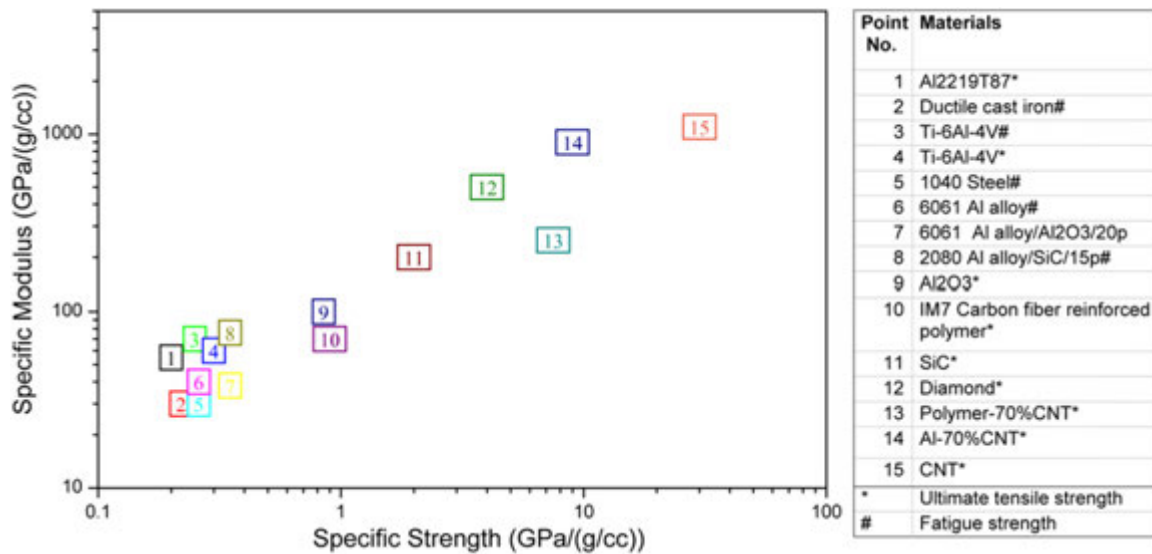


Fig. 1 A typical specific modulus vs. specific strength relation of the different composite, matrix, and reinforcement materials used for aerospace applications.

- Density or bulk density
- Specific strength
- Specific modulus
- Specific stiffness
- Hardness
- Wear resistance
- Coefficient of friction (COF)
- Energy absorption
- Damping capacity
- Thermal conductivity
- Coefficient of thermal expansion
- Hydrophilicity

These characteristics of the composites can easily be tuned by varying the type of matrix, type of reinforcing agents, reinforcement size, shape, content, and distribution. Further, the innovative use of several engineered reinforcements such as nano-sized particles, shape memory alloy (SMA) fibers, hollow balloons, and so on is being considered to develop some next-generation MMCs. However, almost all metallic substances are corrosive in nature (Bobić *et al.*, 2010). Also, MMCs are mostly manufactured at elevated temperatures which helps in the formation of diffusion bond between the reinforcement and matrix interfaces (Lee and Chen, 2005; Cotterill and Bowen, 1993). When the temperature cools down to ambient condition, residual stress generated in the MMCs owing to the mismatched coefficient of thermal expansion (CTE) of each component. This residual stress in the MMCs due to the manufacturing process significantly affects their mechanical properties in any loading mode. Particularly, the residual stress also provokes stress corrosion in MMCs.

Some advanced MMCs, which have recently been developed for use in various automotive components are illustrated in Table 1 (Moghadam *et al.*, 2014).

Sometimes, the reinforced particulate surface needs coating to prevent a chemical reaction by reaction with the matrix material. For instance, carbon fibers (CFs) are widely used in Al or Al alloy matrix composites. But, carbon of CF may react with Al to form a water-soluble aluminum carbide (Al_4C_3) compound on the surface of CF causing a reduction in ductility (Chang *et al.*, 2005). Hence, the carbon fibers are normally protected with Ni (Kar and Sathiyamoorthy, 2009; Kushwaha *et al.*, 2011; Kar *et al.*, 2009), Cu, titanium boride, platinum (Sharma and Kar, 2015a,b), tin (Bhattacharya *et al.*, 2019), lithium (Yadav *et al.*, 2019), hydroxyapatite (Pramanik and Kar, 2011), carbon nanotube (Sharma and Kar, 2014; Singh *et al.*, 2018), etc., coatings to improve the performance of material (Chang *et al.*, 2005; Singh and Balasubramanian, 2009).

Similarly, other fibers used in composites are glass fibers (Rahaman and Kar, 2014, 2011; Rahaman *et al.*, 2010), tungsten fiber (Agarwal *et al.*, 2010), kenthal fiber (Yamini Sarada *et al.*, 2009; Rahaman *et al.*, 2008), etc.

Protective Coatings

The protective coating is applied to the surface of an object, also called substrate to cover it for making functional, decorative, or both. The conventional coatings are generally applied to protect the substrate from corrosion, oxidation, chemical attacks, wear,

Table 1 Advanced MMCs developed for utilization in automotive and other applications

Property	Material	Application
Corrosion	Co-electrodeposited and embedded nanoplatelets of Na-montmorillonite (up to 0.15%) as reinforcement in Cu ₉ -Ni alloys MMCs	Micro-electromechanical system (MEMS) devices (Thurber <i>et al.</i> , 2018)
Wear resistance: High	Silicon carbide (SiC), alumina (Al ₂ O ₃), and/or graphite-reinforced micro and nano MMCs	Bearing surfaces, cylinder liners, pistons, cam shafts, tappets, lifters, rockers, brake components (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)
Wear resistance: Excellent (at 200°C)	Rapidly solidified nanocrystalline Al alloys and Al/SiC nanocomposites (Matrix: Al-Ni-Y-Co, Al-Si-Ni-Ce, and Al-Fe-Ti-M, where M: Cr, Mo, V, Zr)	Automotive industry (Rohatgi and Schultz, 2007; Takagi <i>et al.</i> , 2001)
Wear resistance: Good	Electro-co-deposited Ni-Al ₂ O ₃ nano-particle reinforced MMC coatings	MEMS devices (Rohatgi and Schultz, 2007; Thurber <i>et al.</i> , 2018)
Hardness (2.3 GPa)	Cu-Al ₂ O ₃ (1 wt/wt) nanocomposites (produced by high-pressure torsion technique)	Automotive industry (Rohatgi and Schultz, 2007; Islamgaliev <i>et al.</i> , 2001)
High thermal stability	Al/SiC (20–40 wt% SiC of size 9–38 μm)	Heat sinks for electronics and housings & mirrors for optics, high speed equipment for manufacturing, brake rotors for vehicles (Kuang and Sturdivant, 2017; O'Fallon Casting Pvt. Ltd, 2019)
	Al/SiC (Casting product)-SA301/SA401	Semiconductor processing equipment, Aerospace: heat sink, variable speed refrigerators, inverter, variable frequency drives (VFDs), uninterruptible power system, hybrid vehicles, electric vehicles, and high speed rail train (RichEnergy Technology Co., Ltd, 2010)
High creep strength	Cu-Al ₂ O ₃ (1 wt/wt) nanocomposites (produced by high-pressure torsion technique)	Automotive industry (Islamgaliev <i>et al.</i> , 2001)
Light weight, energy absorption	Fly ash cenosphere- and low-density ceramic microballoon-reinforced syntactic foam MMCs	Crumple zones, pedestrian impact zones, batteries, frame members and reinforcements (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)
Self-cleaning	MMCs with hydrophobic reinforcements, biomimetic coatings, and surface finishes	Water jackets, water pumps, exposed metallic components (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)
Self-lubricating	Micro and nano MMCs incorporating graphite, MoS ₂ , TiB ₂ , hexagonal boron nitride (h-BN), or other solid lubricants	Bearing journals, constant velocity joints, pistons, cylinder liners, gear surfaces (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)
High thermal conductivity	Micro and nano MMCs reinforced with high-conductivity carbon, diamond, or cubic boron nitride (cBN) powder	Cylinder liners, brake components, water passages, catalytic converters, turbo/supercharger components, electronics packaging (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)
Electrical conductivity	Montmorillonite nanoplatelets (up to 0.15%) reinforced Cu ₉ -Ni alloys matrix MMCs	MEMS devices (Thurber <i>et al.</i> , 2018)
Strength High	Micro and nano MMCs reinforced with SiC or Al ₂ O ₃ particles, carbon or Nextel fibers, CNTs, and in situ ceramics	Connecting rods, brake calipers, brake rotors, brake calipers (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)
Tensile strength (680 MPa)	Cu-Al ₂ O ₃ (1 wt/wt) nanocomposites (produced by high-pressure torsion technique)	Automotive industry (Islamgaliev <i>et al.</i> , 2001)
Strength Good	Montmorillonite nanoplatelets (up to 0.15%) reinforced Cu ₉ -Ni alloys matrix MMCs	MEMS devices (Thurber <i>et al.</i> , 2018)
Low cost	MMCs containing fly ash or waste sand as fillers	Intake manifolds, accessory brackets, low-load brackets, oil pans, valve covers, alternator covers, water pumps (Moghadam <i>et al.</i> , 2014; Macke <i>et al.</i> , 2012; Kuang and Sturdivant, 2017)

etc., and also, might be for decoration, texturing, or printing words and images. In general, anticorrosion coatings are used to protect metallic surfaces from corrosive environments by applying paint. It has huge applications such as, automotive industries, new construction components, maintenance, and repair, which includes major refurbishments and onboard maintenance (OBM). The major components of paints are a binder (e.g., epoxy, chlorinated rubber, alkyd, etc.), pigment or extender (e.g., zinc, zinc phosphate, Al, etc.) and solvent (e.g., latex, epoxy, etc.). Oxidation protective coatings are generally applied for temperature applications, particularly on structural materials in aeronautics and aerospace industries. This coating is mainly used to block the contact between oxygen and the substrate materials to achieve the anti-oxidation effect at high temperatures. In this method, generally, ThO₂, Y₂O₃, HfO₂, Al₂O₃, SiO₂, and so on like oxide ceramics are used as coating materials, which have lower oxygen diffusion to inhibit the diffusion of oxygen to the substrate effectively. Chemical protection coatings are mostly used in the chemical and nuclear industries to make the components inert in contact with different harsh chemicals such as concentrated sulfuric acid (H₂SO₄), sodium hypochlorite (NaOCl), hydrochloric acid (HCl), sodium hydroxide (NaOH), and so on. Generally, silicone, polyurethane, novolac, epoxy, and so on are used as chemical resistive coating materials. Wear resistance coating is generally used in metallurgical and many manufacturing industries. The main features of wear resistance coating are high hardness, high fracture toughness, high bond, low porosity, and uniform quality. Normally, tungsten carbide, tungsten carbide cobalt

chrome, titanium carbide, silicon carbide, boron nitride, and so on are used as a wear-resistant coating material, which can be made by different thermal spray techniques. Other advanced protective layer coatings are discussed in the following sections.

Classification of Protective Coating

The life span of metallic objects such as vehicles, the exterior and interior surfaces of buildings, etc., is intended to prolong by the coatings (Ho *et al.*, 2018). The prolonged life span of the protected objects would significantly decrease the required frequency for repair or replacement, in turn, followed by the cut down of long-term environmental impairment and the overall ecological- or carbon-footprint. Protective coating technology on MMCs or any other materials can generally be classified into three types such as (1) painting, (2) coating, and (3) surface treatment as depicted in Fig. 2.

Painting

Painting is done on the materials using only paints by various techniques. Paint generally contains acrylic and/or vinyl resins in liquid form. It flows as a layer followed by the formation of a continuous, flexible, and waterproof film of plastic after the evaporation of solvents, which can be either water or volatile organic compounds (VOCs). The types of painting, the process concepts, and applications are illustrated in Table 2.

Polymeric and pigment-based painting materials hold an enormous global market (Ho *et al.*, 2018). They are available as a solvent or water-based formulations and the main difference between them is the bulk solvent carriers which are the VOCs and water, respectively. However, both are used to protect the metallic surfaces, such as metallic infrastructure, exterior part of the vehicles, interior surfaces of buildings, and so on (Marrion, 2004). The pigment coatings (latexes) or solvent-based paints emit

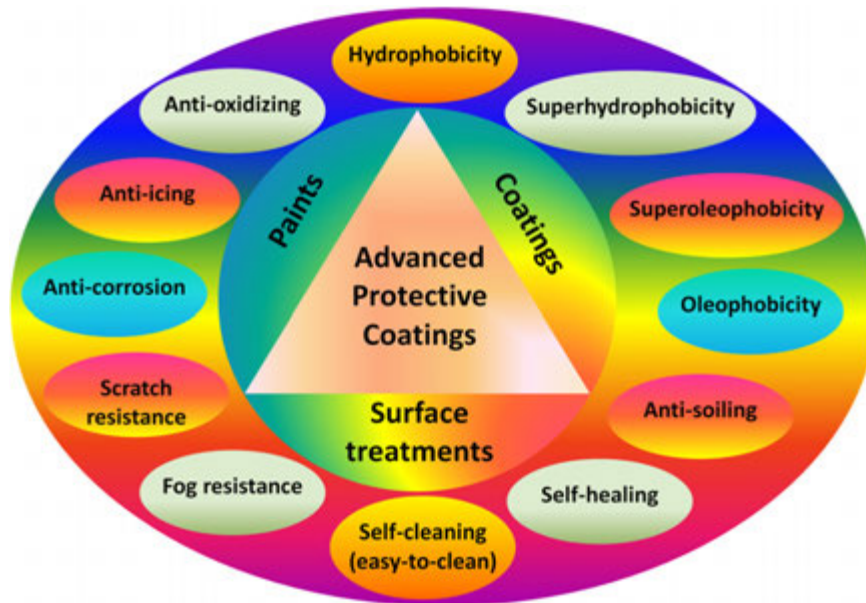


Fig. 2 Advanced protective coatings and their functional properties.

Table 2 Painting methods, concepts, and applications of the process

Painting methods	Concepts of the process	Applications
- Spray, - Electrostatic, - Electrodeposition, and - Powder.	- Organic solvents are evaporated upon drying to form a - continuous, - flexible, and - waterproof film of plastic.	- General uses: - Surface decorations, - Anti-rusting and - Anti-corrosion. - Used as functional painting: - Electro-conductive painting - Non-adhesive painting, and - Lubricating painting.

higher VOC emissions than water-based paints (Matheson, 2002). The mechanisms, advantages, and disadvantages of the solvent-based and water-based coatings are presented in the following section.

- **Solvent-based painting**

In solvent-based and pigmented (paints) based paintings, polymer binder content around 25%–35% (v/v) in a homogeneous solution with an organic solvent of around 50%–75% (v/v) are there in addition to opacity agents or pigments, and many other additives, including bacteriocides or rheology modifiers (Ho *et al.*, 2018; Keddie and Routh, 2010). Polymers, which are generally used for these coatings, should be substantially hydrophobic in nature to render water resistance properties. Further, the painting polymers should have appropriate hardness for providing good mechanical as well as abrasive strengths. The hardness of the painting polymers generally depends on their glass transition temperature (T_g).

- **Mechanism**

In the case of solvent-based paintings, the film formation process starts immediately after the application of paint through the evaporation of organic solvents from the film's surface. It leads the polymer chains to reach close to each other and forms an entangled network structure on the MMCs substrate surfaces (Keddie, 1997). Here, crosslinking agents are usually employed in the formulation of paints to form covalently bonded chains to each other after drying which further improves the mechanical properties as well as the solvent resistance of the coating film. The solvent-based paintings are good as high-quality and durable coatings. They exhibit a smooth film surface on MMCs due to the slow evaporation of the solvent (Ho *et al.*, 2018).

- **Disadvantages**

However, the main disadvantage of the solvent-based coatings is the usage of a huge amount of organic solvents, which can cause environmentally as well as health problems. Further, the solvent poses other risks such as flammability, smog formation, and inhalation (Matheson, 2002; Kim, 2011). Therefore, in new studies, the solvents are released into the atmosphere using some sophisticated coating techniques. However, in most of the applications, the solvents are released directly into the atmosphere or environment and can be absorbed via the skin or lungs (Ho *et al.*, 2018; Kim, 2011; Gaines *et al.*, 2011). On the other hand, water-based is safer for the environment as well as human's or animal's health (Ho *et al.*, 2018).

- **Water-based paint**

Water-based paints contain an aqueous suspension of about 50–300 nm polymer particles and several additives including opacity agents, pigments, coalescing supporters, etc (Keddie and Routh, 2010).

- **Mechanism**

Film formation after the application of paint occurs by water evaporation upon drying. It brings the particles closer in contact. It follows a complex film formation process. In this process, the individual polymer chains diffuse across the interparticle boundaries. It leads to obtain a gradual coalescence of the particles into a coherent film (Ho *et al.*, 2018; Keddie, 1997). The softer polymer particles having a low- T_g are generally used to form an efficient film. Alternatively, high- T_g polymer particles can also be employed however, this approach needs homogeneous heating of the MMCs substrate at an appropriate temperature, which is rarely used (Ho *et al.*, 2018; Paul, 1977).

- **Disadvantages**

Water-based paints work poorly when they are used at low temperatures, particularly, below 10°C due to insufficient inter-particle diffusion of polymer chains and the slow evaporation of water. As a result, the film lacks quality and durability, i.e., poor resistance to mechanical abrasion (e.g., cleaning or scrubbing) and “chalking” defects due to the incomplete coalescence of latex particles (Mason, 1973; Malshe and Waghoo, 2004). Chalking defects are not generally found in solvent-based paints since the polymers are fully dissolved in the organic solvent instead of being suspended. Also, as the film surface holds microscale roughness from the coalesced individual particles, high glossy coatings are normally difficult using water-based paints (Ho *et al.*, 2018; Wang *et al.*, 1992; Carter *et al.*, 2014). Normally for water-based paints, a small amount of VOC is added (e.g., 50 g VOC/L) as the coalescing relief.

Coating or functional coating

Although the coating is a generic term that refers to the substance applied on the outer layer of a substrate, a thin layer of any inorganic functional material on the substrate is termed as a functional coating. The main difference between coating and painting materials is that while the coating is a thin outer layer of an inorganic substance, painting refers to the layer of organic substance on the substrate. For example, inorganics are present as metallic layers or ceramic powders in the coating, while organic materials are present as volatile polymers or plastics in painting.

In functional coatings, the addition of nanocrystalline and nanofiller phases enhances the functional performance (Thurber *et al.*, 2018; Ma *et al.*, 2017; Digital Library, 2019). Types of coating, concepts of the process, and applications are illustrated in Table 3.

The coatings on MMCs can be done by several techniques including, stir casting, hot pressing, physical vapor deposition (PVD), chemical vapor deposition (CVD), diffusion bonding, powder metallurgy, and so on (Thurber *et al.*, 2018; Rosso, 2006). However, some drawbacks are also there for these methods. For example, at high temperatures or under a vacuum in the production, several difficulties have to be faced to control the film thickness and also to maintain the cost (Digital Library, 2019). However, the interest is increasing continuously due to the more availability of cheap nanoparticles.

Table 3 Types of functional coating, concepts, and applications of the process

Functional coating type	Concepts of the process	Applications
Electroplating	Electroplating is a metal coatings (metal plating films) formation process on metallic substrate's surfaces, which are submerged in ionic solutions. The main principle of this method is electrochemical reduction effect.	Applications ranges from micro components to bulk products in: - equipment, - automobiles, - anti-corrosive plating for home appliances - plating for ornaments, and - functional plating.
Electroless plating	- It is a metal or alloy depositing process through electrochemical reactions. - It does not use electricity. - The electroless plating solution contain a reduction agent which substitutes the electricity. - Plating can be done for any kind of material: - metals - plastic - fabrics, and - paper. - It produces more uniform film thickness - However, it is slower than electroplating process. - This process is quite different from chemical plating by substitution reaction.	Mostly, this coating method is used in integrated circuit manufacturing for plating of different metals such as: - cobalt, - nickel, - palladium, or - copper onto one of two types of substrate surfaces (Kellam, 1999)
Vacuum Plating Techniques: - Vacuum Vapor Deposition (VVD), - Sputtering, - Ion Plating, - Ion Nitriding, - Ion Implantation.	Gases or ions of metals, oxides, and nitrides are deposited by vapor deposition in vacuum chambers.	Titanium nitride is used to make gold color coating on MMCs. It is further used for watch casing, decoration and jewelry purposes.
Chemical Coating	- In this process, thin films of sulfide, oxide, and carbides are coated by chemical reactions such as: - Chrome treatment: in post zinc plating, - Parkerizing: phosphate film coating, - Black oxide treatments: on steels, and - Chromic acid coating: on aluminum based materials.	To enhance paint adhesion, chemical coating is used for coloring the metals or alloys to enhance corrosion resistance, and to get priming of surfaces, which are to be painted.
Hot Dipping It is also known as Tempura plating or Dobuzuke plating.	- Products or substrates are dipped in dissolved metals such as: - tin, - lead, - zinc, - aluminum, and - solder - It forms the metallic film on the product's or substrate's surface.	It is most commonly used in zinc plating on steel towers.
Thermal Spraying	- Metals and ceramics (e.g., metal oxides, carbides, or nitrides) powders are sprayed onto surfaces using - flames, - arcs, - plasma streams.	- Typically it is used as below: - spraying for wear prevention - for paint primer based coatings on larger structural objects
Metallic Cementation Double Layer Ion Metallic Cementation	- In metallic cementation, surface alloy layers are formed by covering the surfaces of heated metals via metal diffusion. - Here, both the pre-plated products and the products in powdered metal form to be coated are heated. - Double layer glowing discharge phenomenon is used in double layer ion metallic cementation - Coating depths up to 100 μm can be reached.	Metallic cementation of steel specimens (Zhong <i>et al.</i>, 1982) is done for: - ion-tungstenizing, - ion-molybdenumizing and - ion-chromnickelizing, etc.

Table 4 Types of surface coating treatments, concepts, and applications of the process.

Surface coating treatment method type	Concepts of the process	Applications
Surface Hardening: - Carburizing, - Nitriding, - Induction Hardening - Lase hardening	In this process, the metal surface is altered by surface hardening methods which improve the wear resistance and fatigue endurance.	Surface hardening by carburizing, nitriding, induction hardening, and laser hardening is very common for steel products.
Anodic Oxidation	- In the anodic oxidation method, electrolysis is occurred at the anode in a suitable electrolytic solution to generate thin film on the product's surface. - Here, thin films are generally made of various light metals, such as: - nickel - aluminum, - magnesium, - titanium, and - some oxides. - These coatings (anodizing films) may be porous in nature. - In this treatment, the hard coating can also be developed at a low temperature.	It is used generally for color or dye coating of materials for construction applications, e.g., - vessels - sashes, and so on.

Surface treatment

The surface treatment is a kind of surface modification techniques to achieve required corrosion or oxidation resistance or to create new features on the surface without damaging the desired basic or mechanical properties of the substrate. Here, the surface texturing or restructuring is done by some surface modification techniques using external coating materials. However, in some special cases such as, for specific functional applications, the external substance or functional groups might be used to achieve the targeted performance. Types of surface treatment, concepts of the process, and applications are illustrated in [Table 4](#).

The incorporation of functional groups may include some specific techniques such as oxidation (e.g., ozonization or peroxidation), halogenation (e.g., chlorination or fluorination), nitration, amination, and so on. In general, the functionalization of monomers or polymers onto the substrates' surfaces is done to get a more stable surface structure. The most common techniques used for the incorporation of functional groups to the polymer treated surface are flame treatment, corona treatment, plasma, and radiation, which can increase the surface energy of a biopolymer. However, these techniques may have some disadvantages such as wettability, shelf-life, storage-instability, and so on. For example, the poor stability of the functionalized surface is a terrible problem, particularly in functional biopolymers for in vivo biomedical applications. It may cause unexpected features by alteration of the substrate's properties and/or the degradation profile. As a result, the possibility of undesired side effects may appear.

It has plenty of advanced applications. For example, surface modification techniques can significantly improve the long-term in vivo performance of biomedical implants and provide them with certain biological functions ([Hasan et al., 2013](#); [Moradi et al., 2016](#); [Manna et al., 2016](#); [Pramanik and Kar, 2012](#); [Kar and Pramanik, 2014](#)). Minimum criteria for biomedical surface treatments are:

- Sufficiently high mechanical stability against shearing forces,
- Suitable for cleaning and sterilization,
- Locus and functionally oriented biocompatibility,
- Long-term chemical stability and degradation resistance.

Advanced Protective Coatings and Emerging Coating Technologies

Recently, researchers are extensively trying to explore advanced MMCs such as hollow particle-filled syntactic foams, metal matrix nanocomposites (MMNCs), and functional composites including self-cleaning, self-healing, self-lubricating, etc. There are several surface modification techniques, which are used to improve the resistive performance of materials. Recently, advanced protective coatings have been used to protect the surface and life of components by modifying their surface.

The protection of metallic materials including MMCs is an essential task in any application. The coating on MMCs is necessary not only for preventing them from corrosion ([Thurber et al., 2018](#)), but also for tuning their surface properties such as, hydrophobicity ([Nosonovsky et al., 2011](#)), superhydrophobicity ([Nosonovsky et al., 2011](#); [Tam et al., 2016](#)), superelectrophobicity ([Zhou et al., 2016](#)), oleophobicity ([Nosonovsky and Bhushan, 2012](#)), anti-soiling ([Nair and Dave, 2014](#)), self-healing ([Moghadam et al., 2014](#); [Rohatgi, 2014](#)), self-cleaning ([Moghadam et al., 2014](#)), fog resistance ([Pardo et al., 2006a](#)), scratch resistance ([Yih and Chung, 1997](#)), anti-icing ([Koivuluoto et al., 2017](#)), anti-oxidation ([Xu et al., 2014](#)), and so on, as depicted in [Fig. 2](#) for their various advanced functions.

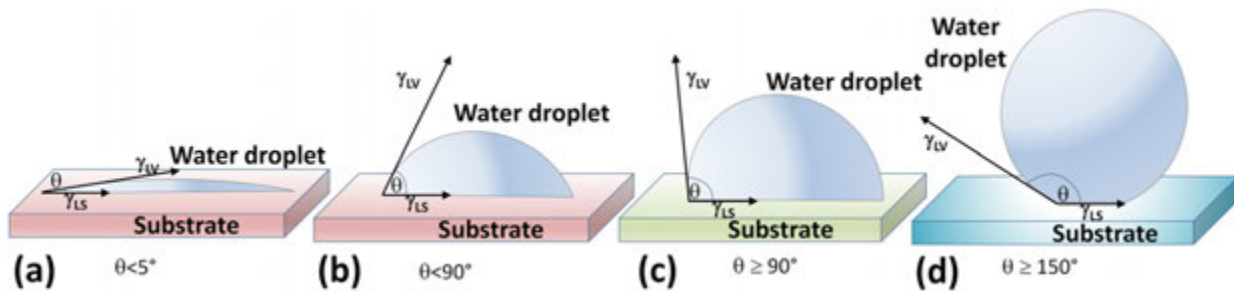


Fig. 3 Comparisons of water contact angle for different surface types: (a) superhydrophilic, (b) hydrophilic, (c) hydrophobic, (d) superhydrophobic properties.

To achieve various functional properties of the metallic or MMC's surface, various coating technologies have been emerged in very recent; some of these are discussed below in the present article.

Hydrophobic Coating

Hydrophobic interaction is very important for understanding several natural phenomena. Since water is the most common solvent, the dissolution property of solutes in water is very interesting to the researchers. The hydrophobic interaction between molecules of hydrophobic solutes, e.g., fat, paraffin, wax, etc., producing from their repulsion of water molecules is liable for their isolation in water (Zhou *et al.*, 2016). Recently, superhydrophobic engineering materials are being designed based on their hydrophobic interaction for a variety of applications. Hydrophobic coating treatments are performed on metals to avoid the absorption of water molecules at the surface. The hydrophobic surface generally has low surface energy. Wetting or hydrophilicity depends on the stability of three-phase interfaces of solid, liquid, and gas. The surface wettability also depends on the roughness of the surface (Wenzel, 1936). A Cassie-Baxter state is a kind state found at the solid-liquid-air interfaces. It occurs in the presence of vapor at the interface of a water droplet and particle's surface owing to surface roughness (Cassie and Baxter, 1944). The contact angles of a water droplet on a hydrophobic surface should be more than 90° as depicted in Fig. 3. The water contact angle is widely calculated by using Young's equation given in Eq. (1) (Young, 1805; Isbilir *et al.*, 2018; Lin *et al.*, 2018).

$$\gamma_{VS} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1)$$

where θ is the contact angle, γ_{SL} is the solid-liquid interface surface tension, γ_{LV} is liquid-vapor interface surface tension, and γ_{VS} is the vapor-solid interface surface tension (Rocha *et al.*, 2009). There have been so many hydrophobic coating techniques developed in recent years and some of them are listed below:

- Lithography technique
- Phase separation technique
- Templating processing technique
- Etching technique
- Sol-gel technique
- Electrostatic spinning technique
- Electrodeposition
- Electro-co-deposition
- Other methods of preparation

The functional molecules can also form bonds to a surface in a self-assembled monolayer (SAM) by changing their properties of surfaces. In hydrophobic coatings, the self-assembled monolayers (SAMs) are prepared by adsorption. The SAMs are such type of molecular assemblies that form spontaneously on the surfaces and organize as ordered domains. A hydrophobic functional coating with SAMs is depicted in Fig. 4. The main features of SAMs-coating as depicted in Fig. 4 are listed below.

- (1) The coating is ultra-thin (≤ 10 nm);
- (2) The self-arrange molecules on the substrate's surface are perfectly homogeneous and capable of complete surface coverage;
- (3) A monolayer has an affinity to the substrate's surface but not for within itself, implying there is no layer stacking or oversizing; and
- (4) Since the monolayer builds a covalent bond with the substrate's surface, it produces high abrasion resistance.

The SAMs-coating thickness may achieve up to the nanometer scale. These coatings can be done on almost all types of materials, such as metals, alloys, ceramics, glass, and polymers. The coating may help to resist abrasion, chemical effect, pH effect, and also physical abrasion. Therefore, in this coating treatment, the coatings can easily make the bond with various products of different classic industrial materials including, complex metal alloys or MMCs.

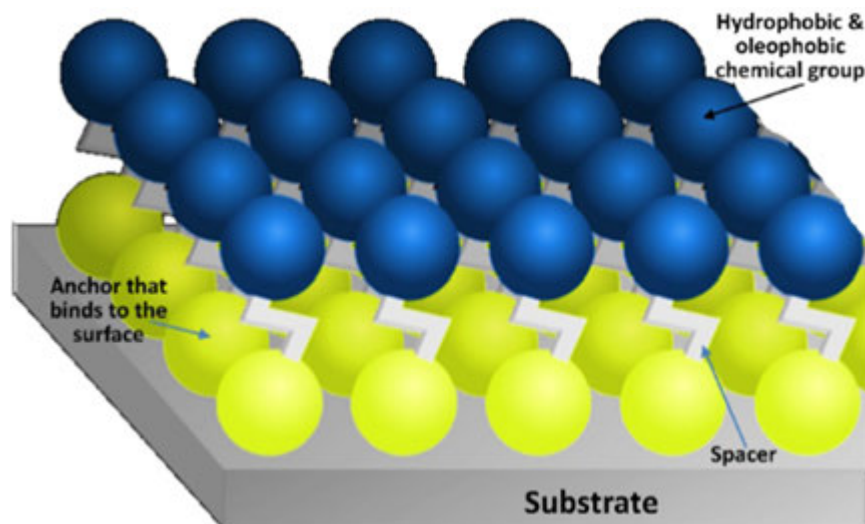


Fig. 4 Hydrophobic functional coating with self-assembled monolayers (SAMs). Reproduced from Surfactis Technologies, 2018. Available from: <https://www.surfactis.com/en/about-us/technology/>

Superhydrophobic Coating

Superhydrophobic coating surfaces are extremely difficult to wet. Since the natural lotus leaves provide superhydrophobicity, it is also known as the “lotus effect”. A superhydrophobic coating on the metallic surface is composed of such water-repellent materials on that water droplets bounce like the backlash of rubber balls. A superhydrophobic coating is a thin layer applied on the surface to strongly repel water molecules. A basic comparison among hydrophilic, hydrophobic, and superhydrophobic surfaces is schematically shown in Fig. 3. The typical water contact angle of a superhydrophobic surface is more than 150° . By little tilting the surface even up to 10° from the horizontal position, the droplet can cause simply bead up and roll off. The superhydrophobic (ultrahydrophobicity) coating materials can able to rebound the entire water droplets after hitting on their surface (Liu *et al.*, 2014; Richard *et al.*, 2002; Khojasteh *et al.*, 2016; George *et al.*, 2016; An *et al.*, 2017). In this context, Richard *et al.* (2002), and Liu *et al.* (2014), showed beautiful illustrations, where a macro-sized water droplet hitting a super-hydrophobic solid and then bouncing like elastomer balls even after tilting the surface at different Weber numbers (W_e) and are schematically depicted in Fig. 5 (Liu *et al.*, 2014; Richard *et al.*, 2002; Khojasteh *et al.*, 2016; An *et al.*, 2017). The Weber number is a characteristic dimensionless quantity and it is the ratio of deforming inertial forces to stabilizing cohesive forces for a liquid flowing through a fluid medium. The W_e can be expressed as Eq. (2).

$$W_e = \frac{\rho u^2 r}{\gamma} \quad (2)$$

where u is the impact velocity, ρ is the density, r is the unperturbed radius of the liquid drop and γ is the surface tension of fluid (water).

This kind of coatings is generally composed of composite materials where one component increases the roughness and the other component reduces surface energy. Superhydrophobic coating surfaces can be made of hydrophobic material having a particular surface roughness. The rough surfaces can be obtained using several techniques as listed below.

- Layer-by-layer and self-assembly,
- Sol-gel processing,
- Etching,
- Electro-spinning method,
- Electrochemical deposition,
- Chemical vapor deposition, and so on.

It can be applied to different metallic substrates. For example, a Cu surface can be patterned with a square lattice of tapered posts and decorated with nanostructures by many researchers (Tran *et al.*, 2013). The post height, cross-section, and width may vary from 500 to 800 μm , 10–100 μm , and 100–300 μm . The post surface can be constructed by chemical etching following of a wire cutting machining (Tran *et al.*, 2013) to generate nanoflower structures of average diameter 2–4 μm . After applying a thin film coating of polymers, including some functional chemicals such as trichloro(1H,1H,2H,2H-perfluorooctyl)silane, a superhydrophobic feature having an apparent contact angle of over 150° is obtained (Liu *et al.*, 2014). Two methods of preparing the superhydrophobic coating are schematically depicted in Figs. 6 and 7 (Mertaniemi *et al.*, 2012).

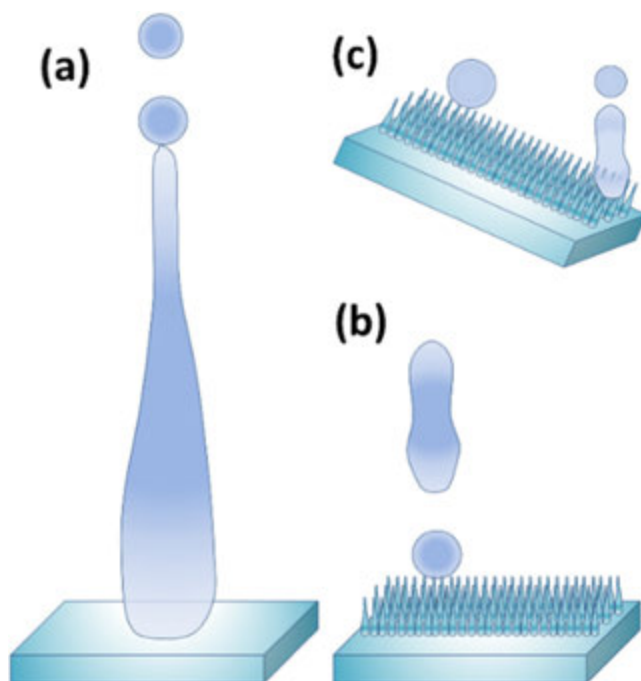


Fig. 5 Different impact view of water droplets with superhydrophobic surfaces: (a) the water drop (at $W_e \approx 18$) becomes highly elongated before detaching from the superhydrophobic surface and gives rise to droplets; (b) a droplet after impacting on the taper-surface at $W_e = 14.1$ with the unique superhydrophobic surface topology at the horizontal position; (c) a droplet after impacting on the taper-surface at $W_e = 31.2$ with the unique superhydrophobic surface topology at tilted position. Redrawn and reprinted with permission from (a) and (b) Khojasteh, D., Kazerooni, M., Salarian, S., Kamali, R., 2016. Droplet impact on superhydrophobic surfaces: A review of recent developments. *Journal of Industrial and Engineering Chemistry* 42, 1–14.

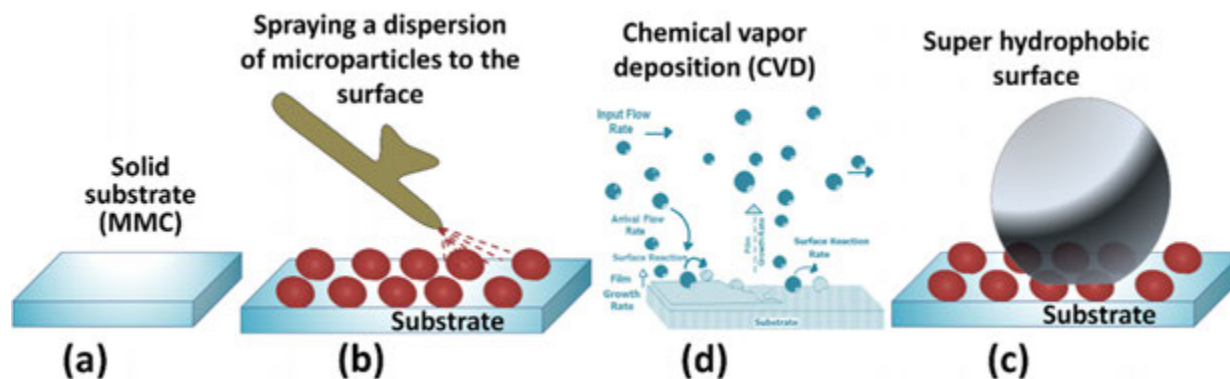


Fig. 6 A lotus-leaf like mimicking of hierarchical topography and the wetting behavior obtained by using spray dispersion followed by CVD. A dispersion of microparticles (e.g., nanofibrillated cellulose (NFC) in ethyl alcohol (C_2H_5OH)) is first sprayed onto a solid surface (e.g., MMCs). Subsequently, the surface is coated with a chemical (e.g., (Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FOTS)) by CVD, to obtain a superhydrophobic coating on the solid surface. Redrawn and reprinted with permission from Mertaniemi, H., Laukkanen, A., Teirfolk, J.-E., Ikkala, O., Ras, R.H., 2012. Functionalized porous microparticles of nanofibrillated cellulose for biomimetic hierarchically structured superhydrophobic surfaces. *RSC Advances* 2 (7), 2882–2886.

In this coating treatment, the coating materials can form bonds easily with different modern and classic industrial products of different substrate materials such as complex metal alloys, MMCs, new generation plastics, vitreous products, and highly sophisticated microelectronic silicon components. The superhydrophobic coating nanoscale treatments significantly can improve their functional characteristics. The superhydrophobic coatings are highly water repellent. Thus, this superhydrophobicity facilitates the treated surfaces easy to clean the deposits and residues retained by water, dirt, and moisture.

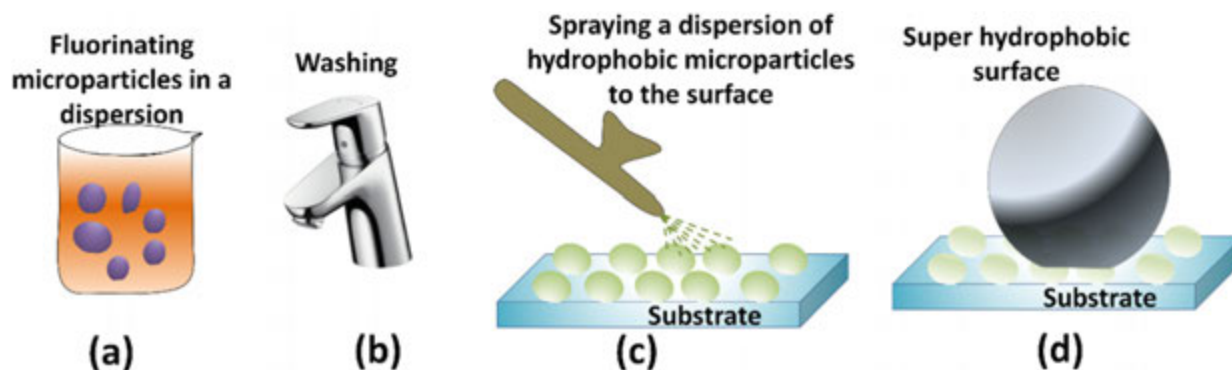


Fig. 7 A lotus-leaf like mimicking of hierarchical topography and wetting properties using spray dispersion. A solution of NFC microparticles dispersed in the toluene medium is first allowed to react with FOTS or fluorinating the microparticles. The dispersed microparticles are subsequently washed to remove extra fluorine and finally, they are sprayed onto the solid substrate to obtain a superhydrophobic coating surface. Redrawn and reprinted with permission from Mertaniemi, H., Laukkanen, A., Teirfolk, J.-E., Ikkala, O., Ras, R.H., 2012. Functionalized porous microparticles of nanofibrillated cellulose for biomimetic hierarchically structured superhydrophobic surfaces. *RSC Advances* 2 (7), 2882–2886.

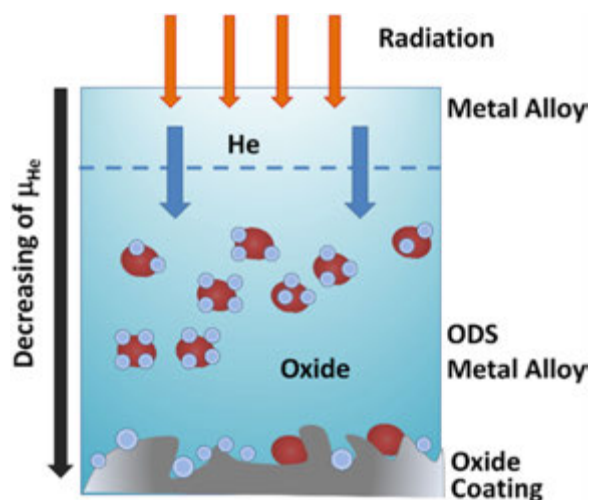


Fig. 8 A new design of radiation-tolerant material based on a layered radiation protection shell governed by an electrophobic interaction; ODS: oxide dispersion strengthened and μ_{He} : chemical potential of helium. *Note:* The μ of the impurities and bubbles keep on decreasing from the first metal alloy layer to the third oxide coating layer (marked by a downward arrow on the left in the vertical axis) owing to their electrophobicity and the interaction between of inert-gas impurity atoms and bubbles. Redrawn and reprinted with permission from Zhou, H.-B., Wang, J.-L., Jiang, W., *et al.*, 2016. Electrophobic interaction induced impurity clustering in metals. *Acta Materialia* 119, 1–8.

Superelectrophobicity Coating

Electrophobic and superelectrophobic interaction concepts are analogous to hydrophobic and superhydrophobic interactions, respectively. It describes the nature of foreign atoms in a metal, i.e., known as “solvent of electrons”. The superelectrophobic interaction presents between the impurities having closed electron shell structure controls their dissolution properties in a metal. The electrophobic or superelectrophobic interaction of different materials such as, He, Be or Ar leads to produce a close-packed cluster having clustering energy (E_c), which is nothing but “electrophobic interaction” energy. It can be proved using first-principles calculations using a universal power-law scaling formula in Eq. (3) (Zhou *et al.*, 2016).

$$E_c \propto N^{2/3} - N \quad (3)$$

where N is the number of atoms dissolved in a free electron gas, as well as metallic (tungsten (W) or Al) lattice. The design of radiation-tolerant material in an electrophobic interaction-based layered radiation protection shell is depicted in Fig. 8 (Zhou *et al.*, 2016).

This futuristic technique significantly progresses the basic insight and ability to predict the behavior of solute impurities in metals. It would be very useful in the coming future to design or modify the metallic surface for metallurgical, energy, and nuclear applications.

Oleophobicity Coating

Oleophobic coatings on the metallic surfaces efficaciously decrease the surface energy and wettability. As a result, the markedly high contact angle is obtained over a range of fluids including, polar (e.g., water or organic solvents) as well as apolar (e.g., hydrocarbon or oil).

The surface energy renders an ability of metallic surfaces to interact with its surrounding environments. It can be computed by measuring the contact angles of at least three different known fluids. The contact angle (θ) is evaluated by measuring a cross-section of a droplet on a flat solid surface and depicted in Fig. 3. The solid surface is considered between the outline of the droplet and the point at which it meets the solid surface.

The oleophobic coatings are highly water, dirt, and moisture repellent. Thus, this coating renders treated surfaces extremely easy to clean specifically the oil, which cannot adhere or smudge to these surfaces. Also, these coatings show dual merits besides their oleophobic nature, so one-ways of a clean cloth or absorbent paper can be cleaned fully.

Anti-Soiling Coating

Anti-soiling coating is a new technology being used to reduce the soiling or making easier to wash. Anti-soiling coatings can be both types either hydrophilic or hydrophobic. The hydrophilic anti-soiling coating has a large surface energy and provides a cleaning action by flowing water (Isbilir *et al.*, 2018). This “self-cleaning” coating is being claimed to facilitate “active” cleaning. It is generally aided by a photoactive titania (TiO_2) layer. The TiO_2 layers can break down organic chains and make the surface easier to clean. However, one disadvantage of TiO_2 materials is that it increases the reflectivity of the cover glass (Kesmez *et al.*, 2009). Since hydrophobic surfaces show low surface energy, they yield fewer adhesion properties for soiling onto the surface. Thus, a hydrophobic anti-soiling coating also helps water droplets to roll off the surface more easily in addition to discharge the dust, dirt, and other forms of soiling (Isbilir *et al.*, 2018). A sol-gel anti-soiling coating process is depicted in Fig. 9.

It has tremendous application in photovoltaic (PV) solar modules where the soiling of solar module cover glass significantly reduces the power output of the module. Soiling creates an accumulation of dust and dirt on PV modules. The soiling causes a

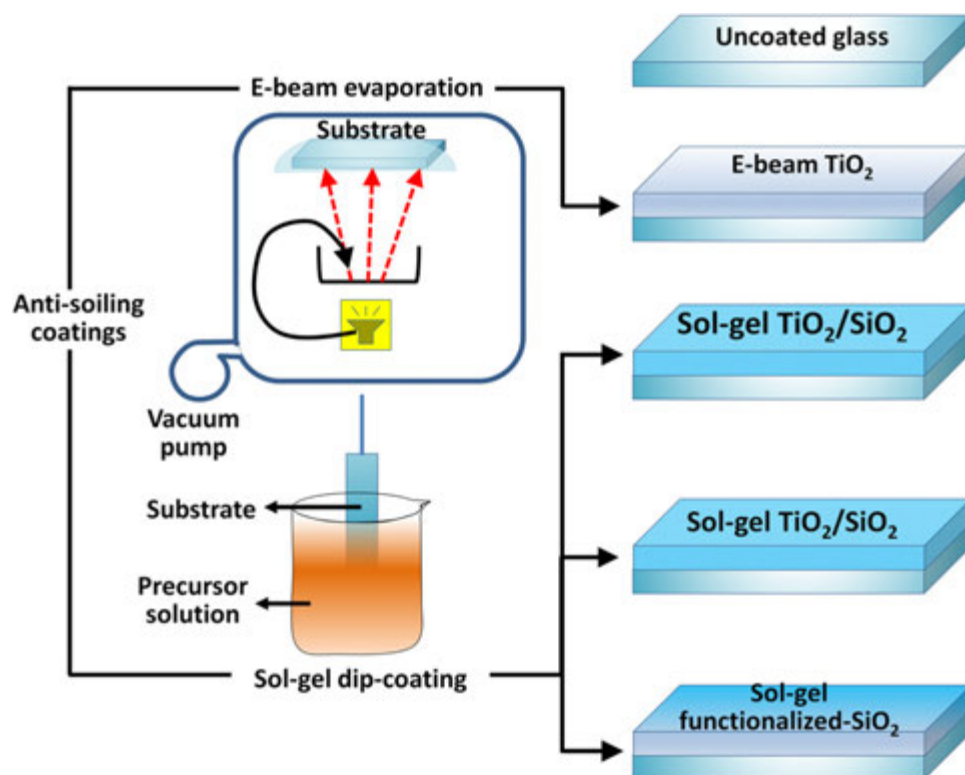


Fig. 9 A schematic of the sol-gel anti-soiling coating process. Redrawn and reprinted with permission from Jesus de, M.A.M.L., Timò, G., Agustín-Sáenz, C., *et al.*, 2018. Anti-soiling coatings for solar cell cover glass: Climate and surface properties influence. *Solar Energy Materials and Solar Cells* 185, 517–523.

terrible loss in PV power plants. Soiling may also cause over 5% reduction in PV system energy output per year in locations without frequent rainfall. Therefore, anti-soiling coatings are applied to the cover glass surface of solar cells to reduce adhesion. It assists the surfaces easier to immaculate and is resilient as well as resistant to environmental damage. So, reducing the average annual energy loss in the PV power plants owing to soiling by even a small amount could have immense value in terms of expanded energy production, particularly for utility-scale projects.

The quality of the anti-soiling coating can be evaluated by the soiling ratio (SR). The SR of a module can be computed for each minute of a data set by dividing the measured maximum power of the module by its expected maximum power when it is cleaned, and soil-free. Thus, the SR can be calculated at each minute, for each photovoltaic module using Eq. (4) (Gostein *et al.*, 2016, 2015).

$$SR = \frac{P_{max}}{P_{max,0} \cdot (1 + \gamma \cdot (T - T_0)) \cdot (G/G_0)} \quad (4)$$

Where, P_{max} = measured maximum power of the module in its soiled state, $P_{max,0}$ = expected calibration value for the module's maximum power when clean and at a reference condition (e.g., standard test condition, STC), γ = temperature coefficient of maximum power, T = measured module temperature, T_0 = module temperature at the reference condition (e.g., 25°C at STC), G = measured plane-of-array irradiance determined from the clean reference cell, and G_0 = irradiance at the reference condition (e.g., 1000 W/m² at STC) (Gostein *et al.*, 2015).

Self-Healing Coating

Self-healing coating is a type of coatings that can autonomically repair and prevent surface attacks such as corrosion of the underlying substrate. It can be created through homogeneous dispersion of microencapsulated healing agents in a polymeric film. These healing agents are normally released into the damaged region to passivate the substrate during self-healing the damage. This self-healing coating approach is quite common. It is efficient for both models and industrial coating systems. A self-healing polymer coating material is depicted in Fig. 10(a) (Cho *et al.*, 2009; Zhang and Li, 2016). In this process, the self-healing coating consists of a microencapsulated catalyst (whitish blue) and phase-separated healing agent droplets (accent red) in a matrix (orange) on a metallic substrate (accent aqua). After the damage to the coating layer, it releases catalyst (yellow) and healing agents (gray). Then, the mixing of healing agents and catalysts occurs in the damaged part. Finally, the damage healed by cross-linked polymer, protecting the substrate from its surrounding environment (Cho *et al.*, 2009). In Fig. 10(b), schematic representation of a self-healing process of an MMC subjected to tensile loading is depicted (Moghadam *et al.*, 2014; Zhang and Li, 2016). When a self-healing MMC tensile bar (ash) containing aligned SMA wires (brick-red) fails in tension, the SMA wires form a bridge in the crack (II); but upon heating (red-coils ON), the SMA wires pull the edges of the crack together and the matrix partially melts (III); Due to cooling (gray-coils OFF), the bar results in solidification of the matrix and bonding of the crack surfaces (IV). Redrawn and reprinted with permission from Zhang, P., Li, G., 2016. Advances in healing-on-demand polymers and polymer composites. Progress in Polymer Science 57, 32–63.

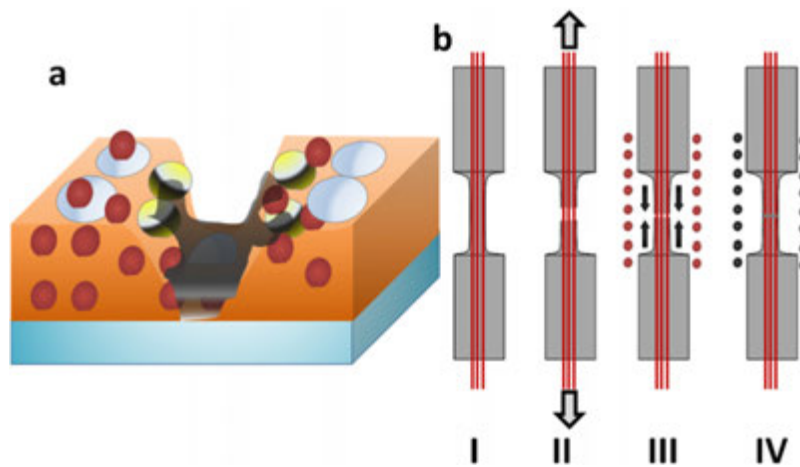


Fig. 10 (a) A self-healing polymer coating material. (b) A self-healing MMC tensile bar (ash) containing aligned SMA wires (brick-red) (I); the tensile bar fails in tension the SMA wires form a bridge in the crack (II); but upon heating (red-coils ON), the SMA wires pull the edges of the crack together and the matrix partially melts (III); Due to cooling (gray-coils OFF), the bar results in solidification of the matrix and bonding of the crack surfaces (IV). Redrawn and reprinted with permission from Zhang, P., Li, G., 2016. Advances in healing-on-demand polymers and polymer composites. Progress in Polymer Science 57, 32–63.

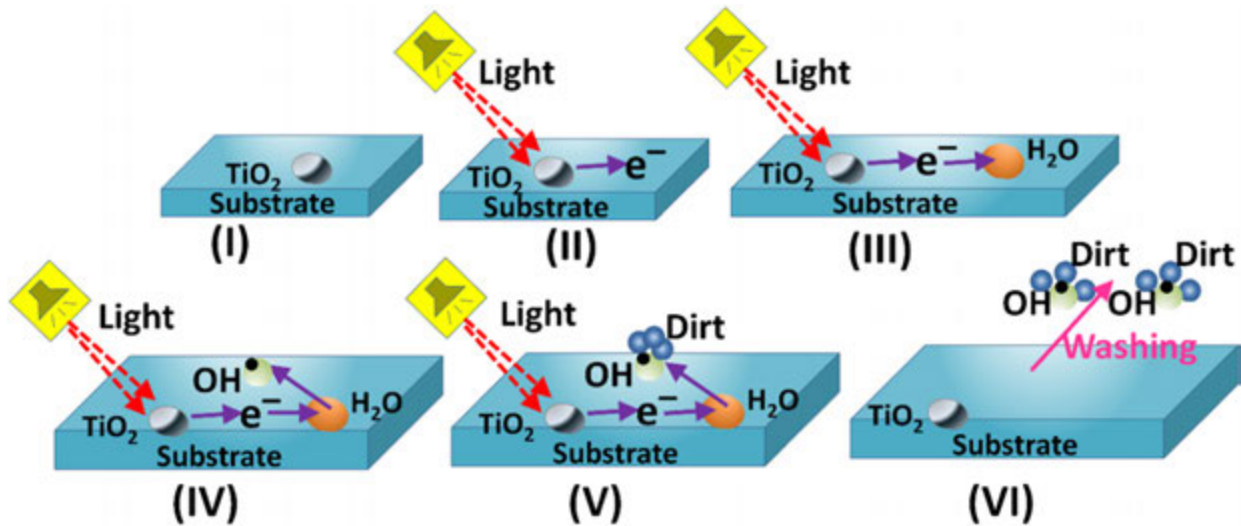


Fig. 11 The principle of the hydrophilic self-cleaning coating. (I) TiO_2 coating MMC substrate, (II) Electrons of TiO_2 particles activated in presence of light (especially, via UV illumination), (III) The electrons of the TiO_2 -surface react with water molecules, (IV) The electrons evolved from the TiO_2 -surface split water molecules into hydroxyl radicals (OH^*), (V) These radicals react with organic dirt particles and break into smaller particles, (VI) The smaller particles are easily washed away by water. Redrawn and reprinted with permission from Nakajima, A., Koizumi, S.-I., Watanabe, T., Hashimoto, K., 2000. Photoinduced amphiphilic surface on polycrystalline anatase TiO_2 thin films. *Langmuir* 16 (17), 7048–7050.

hydrophobicity, can be analyzed by using optical tensiometers. The efficiency of a hydrophobic self-cleaning coating depends on the chemical composition and roughness of the surface and also on the adhesion of dirt particle to water droplet (George *et al.*, 2016; Sakka and Kozuka, 2005). The hydrophilic self-cleaning coatings are prepared based on the photocatalysis process. When the photocatalysts are exposed to light, they can break down the impurities. It is used in self-cleaning windows, which are commercially available. This kind of window generally cleans its surface in two ways. When the organic dirt is absorbed onto the window surface, it is broken down chemically by photocatalysis. Subsequently, the broken dirt particles are washed out by water by creating sheets owing to the low contact angles. TiO_2 is also a commonly used coating for hydrophilic self-cleaning surfaces owing to its favorable physical and chemical properties. Also, TiO_2 is non-toxic and chemically inert in dark conditions. It is also cheap, easy to handle, and widely well-known as in household chemicals (e.g., pigment in cosmetics and paint). The strong oxidation power and superhydrophilic characteristics of TiO_2 make it a potent material that is used as a self-cleaning coating especially in outdoor uses. The self-cleaning effect of a TiO_2 coated MMC substrate is illustrated in Fig. 11 (Nakajima *et al.*, 2000).

Fog-Resistance Coating

A small droplet of condense water on the substrate from the surrounding atmosphere may create several problems in many sophisticated instruments and applications. Due to the change in temperature and humidity, water condensates for droplets formation onto the substrates create several problems including, corrosion on metallic substances, obscured vision for glassy products, and so on causes several safety issues. Therefore, prevent fogging of interior helm visor during spacewalks was originally developed by national aeronautics and space administration (NASA).

The fogging problem is a very big issue in the world which causes a huge number of accidents and transport delays around the globe every year, particularly in the winter season. Fog-resistance coating component enhances permanent scratch-resistant properties and improves other surface characteristics. These anti-fog coating materials can be applied for thermoforming, including shaping and molding, without the annihilation of their original properties. Anti-fog coatings can prevent the buildup of mist on a variety of materials. Usually, fog appears due to the condensation of moisture on a solid surface (hydrophobic) and subsequently becomes tiny droplets, which can scatter lights. It is expected that a highly hydrophilic material absorbs condensed moisture. However, the highly hydrophilic materials become saturated very fast and thus, make it poor anti-fog coatings. Therefore, modification of such hydrophilic materials is essential. This modification is done with proper surfactants that include a domain of hydrophilic and hydrophobic segments and causes condensate to spread. It maintains the visibility of a coated substrate (La Casse and Creasy, 1999). The anti-fog mechanisms of hydrophilic coating material coated on MMCs substrate are depicted in Fig. 12.

Some important features of anti-fog products are:

- It is easy to apply even by spraying,
- No curing is needed,
- No permanent bonding or chemical bonding with the substrate is required,
- There is a saturation of coating with water,
- It is also cheap.

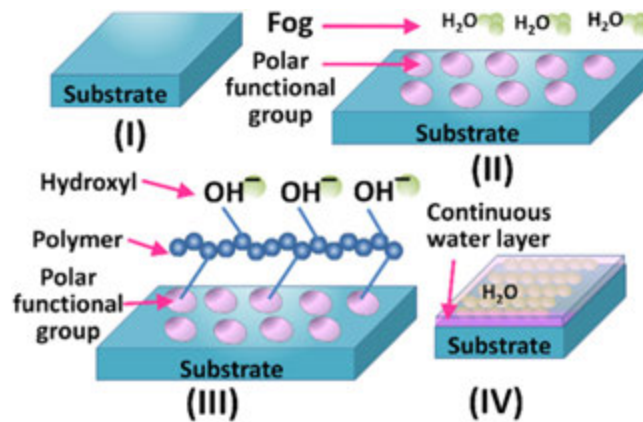


Fig. 12 Mechanisms of anti-fog coating on MMCs substrate: (I) substrate; (II) coating with an anti-fog film comprising water (H_2O) friendly polar functional groups such as ($-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$, $-\text{PO}$, etc) on the substrate and exposed in a fog environment; (III) bonding with hydroxyl (OH^-) group of water from the foggy environment via an optional polymer layer; (IV) a continuous (no disruption) thin film of water formed on the substrate's surface.

Pardo *et al.* (2006a), studied the corrosion properties of different fog-resistance coated silicon carbide particle (SiCp) reinforced Al matrix MMCs in salt fog environment. Kinetic mechanisms of corrosion for the Al-MMCs modified by cerium (Ce) based transition or electrolysis coating in a fog environment of a neutral salt was evaluated by gravimetric analyses as per ASTM B 117 standard method. Pardo *et al.* postulated that the kinetic constant or corrosion reaction rate constant can be reduced by the addition of SiCp, which reduces the surface area of the Al matrix. Whereas, the kinetic constant can be increased by the addition of Cu and Ni owing to the formation of an Al/Cu, Ni galvanic couple. But, Ce-based surface treatment reduced the kinetic constants by inhibition of cathodic reaction, which annihilated the growth rate of corrosion products (i.e., a layer of bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)) and stabilizing the Al_2O_3 of original protective layer (Pardo *et al.*, 2006b). As a result, the corrosion resistance of the materials was increased. This effect was more prominent when the Ce-modified fog-resistance coated Al-MMC was carried out by electrolysis.

Scratch Resistance Coating

To improve the durability of the MMCs, the scratch-resistant property is very important. Since many metal matrices are very soft in nature, for example, Cu, Mg, Al, and so on, scratch resistance coating on their composite plays a crucial role particularly in the engineering applications where high wear resistance property is desired.

Scratch resistance coating on MMCs can be done by several methods as listed below:

- Electro-co-deposition (ECD),
- High-velocity oxygen fuel (HVOF),
- Thermal spraying,
- Hot isostatic pressing (HIP), etc.

Some aluminum 7075 based components, such as engine pistons experience severe wear while working under fairly high temperatures. Such components require adequate surface treatment to increase the scratch or wear resistance by lowering the friction coefficient (Devaney and Senthilvelan, 2014). The scratch-resistant coating can be done by the electro-co-deposition technique as depicted in Fig. 13 (Devaney and Senthilvelan, 2014).

ECD is a more beneficial technique in comparison to other coating methods, such as HVOF, HIP or thermal spraying, owing to its capability of continuous processing, faster deposition, homogeneous distribution, normal working pressure, low maintenance, ability to deal complex geometry, and reduced waste generation (Devaney and Senthilvelan, 2014). ECD is an effective technique to produce coatings on MMCs through the co-deposition of metallic and non-metallic particles along with pure metals or alloys. It can also significantly improve the corrosion resistance and tribological properties of the substrate. Recently, the co-deposition of ceramic particles such as SiC, WC, TiC, TiO_2 , Cr_2O_3 , Al_2O_3 , etc., along with metalizing (e.g., Ni plating, etc.) have been used to improve the wear resistance of plated parts (Szczygieł and Kołodziej, 2005; Hu and Chan, 2006; Aal *et al.*, 2007). The tribological characteristics of the coating using these methods mainly depend on the size, amount, and distribution of reinforced particles (Thiemig *et al.*, 2007). The surface morphology can be affected by the electroplating parameters, including current density, pH, temperature, bath composition, and stirring speed (Kilic *et al.*, 2013). It has also been found that the wear-resistance increases with increasing the SiC contents in the Ni/SiC composite coatings. Recent studies reveal that in the presence of SiC particles, the normal growth of Ni crystals gets hindered, thus develops more inter-crystalline bonding (Baghal *et al.*, 2012). But in the case of micron-sized particles, the co-deposition of homogeneous deposits is highly ambiguous due to the greater tendency in the agglomeration of the microparticles. The non-homogenous ECD may lead to reduce the wear-resistance of the coated substrate. In this context, since titanium diboride (TiB_2) is also famous due to its relevant properties such as, for its stiffness, hardness,

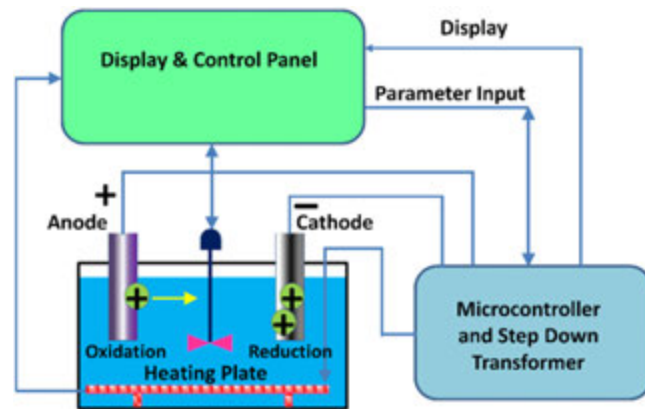


Fig. 13 A schematic electro-co-deposition (ECD) technique for scratch-resistant coating. Redrawn and reprinted with permission from Devaneyan, S.P., Senthilvelan, T., 2014. Electro co-deposition and characterization of SiC in nickel metal matrix composite coatings on aluminium 7075. *Procedia Engineering* 97, 1496–1505.

electrically, and thermally conductive, it can be used as a potent coating material on the soft MMCs. In a coated filler method, the surface of the hard particles (e.g., TiB_2 platelets) is first metalized by electroless plating process with matrix metal (like Cu) and subsequently electroplated with Cu to obtain metal-coated hard particles with desired concentration (Yih and Chung, 1997).

Anti-Icing Coating

Since anti-icing surfaces are profoundly hydrophobic, they are extremely difficult to wet. Applying a superhydrophobic coating on MMCs-surfaces converts them into a highly liquid and water repellent, easy to clean, and significantly boosts their anti-icing performance. Anti-ice coating reduces ice and wet-snow adhesion (sometimes: up to 80%) to the underlying substrates. It is used to prevent dangerous ice built up on the components. The advanced coating materials, for example, SuperAi (commercial name, NEI Corporation), can be applied directly to versatile substrate materials, including plastics, metals, MMCs, glass, concrete, and ceramics. It has very vital applications in engineering. A low-viscosity formulation material, which can spread quickly on the surface, is generally used as an anti-icing coating material and applied on the substrate's surface. It can even flow over surfaces of the complex structured components. Then, it quickly cures under ambient conditions.

According to some studies, the two key factors in obtaining superhydrophobicity for anti-ice properties are (1) lower surface free energy and (2) microscopic rough structures. It is to be informed that such a rough structure not only increases the surface superhydrophobicity significantly but also creates some anti-icing performances under certain conditions (Hasan *et al.*, 2013). The anti-icing property can be evaluated by the main two concepts: (1) icing-delay time and (2) ice-adhesion strength (Lin *et al.*, 2018). The ice-adhesion strength (τ) is calculated by using the Eq. (5):

$$\tau = F/A \quad (5)$$

where F is the critical force and A is the contact area of ice-column with the sample surface.

The adhesion of ice or wet-snow on the surfaces of various components of automobiles, aircraft, and so on results several serious aviation accidents and also gives a fatal threat to the safety of the crafts. In this context, an air crashing of flight (China Eastern Airlines MU5210 going from Baotou to Shanghai in November 2004) was suspected to be held by undesired ice-accumulation on the aircraft's surfaces. It caused a huge loss of lives as well as serious economic issues (Lin *et al.*, 2018). In frosting weather, the ice accretion caused a loss in control on operating speed and thereby the plane lost its lift. As a result, the ice reduced the critical angle of attack, particularly during the formation of the ice, at the leading edges of wings.

Anti-Oxidation Coating

Anti-oxidation is extremely useful for the utilization of MMCs in high-temperature applications. There have been numerous methods including, anti-oxidation coatings produced by various painting, coating, or surface treatments developed by several researchers particularly for protecting the metallic components from low-temperature oxidation, thermal oxidation, or high-temperature oxidation, corrosion, residual stress formation, and so. For example, Fu *et al.* (2017) had found several factors responsible for the oxidation of carbon steels based MMCs:

- The high silicon (Si)-coating can enhance the resistance to oxidation.
- The blisters formation can reduce oxidation.
- The solid-phase sintering reactions also can enhance anti-oxidation properties.
- Si and Cr played a key role in oxidation resistance.
- Anti-oxidation coating can significantly reduce the mass loss due to the oxidation of steel (nearly up to 85%).

Due to anti-oxidation coatings, several phases are developed on the surfaces of the substrate, responsible for reducing the further oxidation reaction to the substrate. Transition metal disulfides (MS_2 where M is molybdenum or tungsten) are used as anti-oxidation coatings on MMCs and also act as solid lubricants in various space motion mechanisms, which are very important for tribological applications (Xu *et al.*, 2014; Wang and Gao, 2014).

Particularly in high-temperature applications, the ceramic coatings are very widely used for reducing the oxidation of MMCs components. The main concept of applying ceramic coatings onto heat engine components is to provide improved oxidation protection. It also imparts corrosion protection for the substrate of MMCs and alloys. The anti-oxidation ceramic coatings also can be used to tailor the insulation, thermal conductivity, electrical conductivity, coefficient of thermal expansion (CTE), reflectivity, diffusivity, properties of MMCs, or alloys by using different ceramic coating produced by many conventional and advanced techniques (Pramanik *et al.*, 2017). The different methods are used to coat the surface of metals are (Thiruseelvam, 2015; Pavan and BR, 2018):

- Physical vapor decomposition (PVD) coating
- Chemical vapor decomposition (CVD) coating
- Ion coating
- Splash coating
- Electron beam evaporation (EBE) coating
- Flame spray (FS) coating
- Plasma spray (PS) coating
- Plasma sprayed ceramic (PSC) coating
- Sol-gel (SG) coating
- Detonation gun (DG) coating
- Reactive ion (RI) coating
- Hot isostatic press (HIP) coating
- Laser surface alloying (LSA) coating
- High-velocity oxy-fuel (HVOF)
- Thermal barrier (TB) coating

The thermal barrier coating is particularly very important for engine components. With a fuel additive, it drastically reduces exhaust emission (Sathiyagnanam *et al.*, 2010). Mild improvement in the thermal efficiency of the engine observes owing to the influence of thermal barrier coating (TBC). The smoke level can be higher in TB coated engine. The NO_x emission can be reduced up to 500 ppm for TB coated engine comparing with standard engines. Upon the addition of fuel-additives to the TBC engines, the NO_x emission can further be reduced to 100 ppm. The heat release rate can slightly be decreased owing to the influences of either TB coating lonely or TB coating along with fuel-additives (Sathiyagnanam *et al.*, 2010; Haşimoğlu *et al.*, 2008).

Some ceramic coatings on mild steel substrates are illustrated in Table 5.

Table 5 Some ceramic coatings on metallic substrates

Year	Coating substrate	Coating material	Method
1992	Different metals (Cu, Ni, Fe, Al)	ZrO_2 , SiO_2 , TiO_2 and $B_2O_3-SiO_2$	Sol-gel dip-coating method (Innocenzi <i>et al.</i> , 1992)
1997	Mild Steel	A mixture of α , δ , and γ phases of Alumina, and 100% $(Al-Cr)_2O_3$ alumina-chromia annealed up to 1300°C	Plasma spraying (Pavan and BR, 2018; Chraska <i>et al.</i> , 1997)
1998	Mild Steel ball indenter	ZrO_2 -8 mol% Y_2O_3 , i.e., yttria stabilized zirconia (8YSZ)	Plasma spraying (Pavan and BR, 2018; Wallace and Ilavsky, 1998)
2002	Steel surfaces	Zn and Zn-Al coatings	Electrolytic plasma processing (Meletis <i>et al.</i> , 2002)
2004	Mild Steel	$Ni-Al_2O_3$	Dip Coating (Pavan and BR, 2018; Marikkannu <i>et al.</i> , 2004)
2005	Metals (copper)	$Ni-Al_2O_3$ composite	Electrodeposition (Bahrololoom and Sani, 2005)
2008	Mild Steel	Alumina	Sol-gel method (Ruhi <i>et al.</i> , 2008)
2010	Mild Steel	Al/SiCp	Low cost oxy-acetylene thermal spraying (Torres <i>et al.</i> , 2010)
2010	Medium carbon steel disk and stainless steel rod	Nanostructured ZrO_2 -3 mol% Y_2O_3 , i.e., yttria stabilized zirconia (YSZ) coatings	Air plasma spraying (Liang <i>et al.</i> , 2010)
2013	Mild Steel	VC - Cr_7C_3 ceramic	Laser cladding surface treatment (Wu <i>et al.</i> , 2013)
2016	Ni based superalloy	Al_2O_3 anti-oxidation coatings	Cathode plasma electrolytic deposition (CPED) (Wang <i>et al.</i> , 2016)
2018	90:10 Cu-Ni alloy	Montmorillonite (Mt) nanoplatelets embedded into the metallic matrix from electrolytic baths comprising 0.05, 0.10, and 0.15% Mt	Coelectrodeposited (Thurber <i>et al.</i> , 2018; Digital Library, 2019)

Concluding Remarks

In this article, advanced protective coating technologies for different materials including, metals, alloys, and MMCs have been discussed. It has been found that almost all kind of solid materials such as metallic, ceramic, cermet, some polymeric, and their composite materials in the form thin film of powder, wire, rod, grain alteration or texture can be coated with proper technology to tune their most advanced functional properties such as hydrophobicity, superhydrophobicity, superoleophobicity, oleophobicity, anti-soiling, self-healing, self-cleaning, fog resistance, scratch resistance, anti-icing, anti-oxidation, and so many using suitable coating technology. Finally, it can be concluded that the superhydrophobic surfaces using emerged technologies such as superoleophobicity coating, anti-soiling coating, self-healing coating, self-cleaning coating, fog-resistance coating, and so on, would have tremendous functional sophisticated applications in future generations.

References

- Aal, A.A., Zaki, Z., Hamid, Z.A., 2007. Novel composite coatings containing (TiC–Al₂O₃) powder. *Materials Science and Engineering: A* 447 (1–2), 87–94.
- Agarwal, S., Sarada, B.Y., Kar, K.K., 2010. The fabrication of carbon-nanotube-coated electrodes and a field-emission-based luminescent device. *Nanotechnology* 21 (6), 065601.
- Allison, J.E., Cole, G.S., 1993. Metal-matrix composites in the automotive industry: Opportunities and challenges. *JOM* 45 (1), 19–24.
- An, A.K., Guo, J., Lee, E.-J., *et al.*, 2017. PDMS/PVDF hybrid electrospun membrane with superhydrophobic property and drop impact dynamics for dyeing wastewater treatment using membrane distillation. *Journal of Membrane Science* 525, 57–67.
- Ataollahi Oshkour, A., Pramanik, S., Shirazi, S.F.S., *et al.*, 2014. A comparison in mechanical properties of cermets of calcium silicate with Ti-55Ni and Ti-6Al-4V alloys for hard tissues replacement. *The Scientific World Journal* 2014, 616804.
- Baghal, S.L., Sohi, M.H., Amadeh, A., 2012. A functionally gradient nano-Ni–Co/SiC composite coating on aluminum and its tribological properties. *Surface and Coatings Technology* 206 (19–20), 4032–4039.
- Bahrololoom, M., Sani, R., 2005. The influence of pulse plating parameters on the hardness and wear resistance of nickel–alumina composite coatings. *Surface and Coatings Technology* 192 (2–3), 154–163.
- Barnes, S., Pashby, I.R., Mok, D.K., 1996. The effect of workpiece temperature on the machinability of an aluminum/SiC MMC. *Journal of Manufacturing Science* 118 (3), 422–427.
- Bhattacharya, P., Lee, J.H., Kar, K.K., Park, H.S., 2019. Carambola-shaped SnO₂ wrapped in carbon nanotube network for high volumetric capacity and improved rate and cycle stability of lithium ion battery. *Chemical Engineering Journal* 369, 422–431.
- Bobić, B., Mitrović, S., Babić, M., Bobić, I., 2010. Corrosion of metal-matrix composites with aluminium alloy substrate. *Tribology in Industry* 32 (1), 3–11.
- Böhm, H.J., Eckschlagner, A., Han, W., 2002. Multi-inclusion unit cell models for metal matrix composites with randomly oriented discontinuous reinforcements. *Computational Materials Science* 25 (1–2), 42–53.
- Carter, F.T., Kowalczyk, R.M., Millichamp, I., Chainey, M., Keddie, J.L., 2014. Correlating particle deformation with water concentration profiles during latex film formation: Reasons that softer latex films take longer to dry. *Langmuir* 30 (32), 9672–9681.
- Cassie, A., Baxter, S., 1944. Wettability of porous surfaces. *Transactions of the Faraday Society* 40, 546–551.
- Chang, K.-C., Matsugi, K., Sasaki, G., Yanagisawa, O., 2005. Effect of fiber surface structure on interfacial reaction between carbon fiber and aluminium. *JSME International Journal Series A Solid Mechanics and Material Engineering* 48 (4), 205–209.
- Cho, S.H., White, S.R., Braun, P.V., 2009. Self-healing polymer coatings. *Advanced Materials* 21 (6), 645–649.
- Chraska, P., Dubsky, J., Neufuss, K., Pisacka, J., 1997. Alumina-base plasma-sprayed materials part I: Phase stability of alumina and alumina-chromia. *Journal of Thermal Spray Technology* 6 (3), 320–326.
- Clyne, T., Withers, P., 1995. *An Introduction to Metal Matrix Composites*. Cambridge university press.
- Cotterill, P., Bowen, P., 1993. Fatigue crack growth in a fibre-reinforced titanium MMC at ambient and elevated temperatures. *Composites* 24 (3), 214–221.
- Devis, R., Yellup, J., Subramanian, C., 1998. Metal-matrix composite coatings by PTA surfacing. *Composites Science and Technology* 58 (2), 299–309.
- Devaneyan, S.P., Senthilvelan, T., 2014. Electro co-deposition and characterization of SiC in nickel metal matrix composite coatings on aluminium 7075. *Procedia Engineering* 97, 1496–1505.
- Digital Library, 2019. High temperature blankets for the production of synthetic fuels. Available from: <https://nam03.safelinks.protection.outlook.com?url=http%3A%2F%2Fwww.digital-library.unt.edu%2F&data=02%7C01%7CMRW-MTCP-S%40elsevier.com%7C729771de05eb44d23c5608d803018f0c%7C9274ee3f94254109a27f9fb15c10675d%7C0%7C0%7C637262653379825278&data=70Ds5%2FPohBDTgN2PUPrDQjE5MpQGpCeLTsZEnbYr1s%3D&reserved=0>.
- Fu, G.Y., Wei, L.Q., Zhang, X.M., *et al.*, 2017. A high-silicon anti-oxidation coating for carbon steel at high temperature. *Surface and Coatings Technology* 310, 166–172.
- Gaines, L.G., Fent, K.W., Flack, S.L., *et al.*, 2011. Factors affecting variability in the urinary biomarker 1, 6-hexamethylene diamine in workers exposed to 1, 6-hexamethylene diisocyanate. *Journal of Environmental Monitoring* 13 (1), 119–127.
- George, J.E., Rodrigues, V.R., Mathur, D., Chidangil, S., George, S.D., 2016. Self-cleaning superhydrophobic surfaces with underwater superaerophobicity. *Materials & Design* 100, 8–18.
- Gostein, M., Düster, T., Thuman, C., 2015. Accurately measuring PV soiling losses with soiling station employing module power measurements. In 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC). IEEE.
- Gostein, M., Stueve, B., Brophy, B., *et al.*, 2016. Soiling measurement station to evaluate anti-soiling properties of PV module coatings. In 2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC). IEEE.
- Hasan, J., Webb, H.K., Truong, V.K., *et al.*, 2013. Selective bactericidal activity of nanopatterned superhydrophobic cicada *Psaltoda claripennis* wing surfaces. *Applied Microbiology and Biotechnology* 97 (20), 9257–9262.
- Haşimoğlu, C., Ciniviz, M., Özsert, İ., *et al.*, 2008. Performance characteristics of a low heat rejection diesel engine operating with biodiesel. *Renewable Energy* 33 (7), 1709–1715.
- Ho, J., Mudraboyina, B., Spence-Elder, C., *et al.*, 2018. Water-borne coatings that share the mechanism of action of oil-based coatings. *Green Chemistry* 20 (8), 1899–1905.
- Hu, F., Chan, K., 2006. Equivalent circuit modelling of Ni–SiC electrodeposition under ramp-up and ramp-down waveforms. *Materials Chemistry and Physics* 99 (2–3), 424–430.
- Innocenzi, P., Guglielmi, M., Gobbin, M., Colombo, P., 1992. Coating of metals by the sol-gel dip-coating method. *Journal of the European Ceramic Society* 10 (6), 431–436.
- Isbilir, K., Lisco, F., Wornack, G., Abbas, A., Walls, J.M., 2018. Testing of an anti-soiling coating for PV module cover glass. In: *Proceedings of the 2018 IEEE 7th World Conference on Photovoltaic Energy Conversion (WCPEC) (A Joint Conference of 45th IEEE PVSC, 28th PVSEC & 34th EU PVSEC)*. IEEE.
- Islimgaliyev, R., Buchgraber, W., Kolobov, Y.R., *et al.*, 2001. Deformation behavior of Cu-based nanocomposite processed by severe plastic deformation. *Materials Science and Engineering: A* 319, 872–876.

- Kar, K.K., Sathiyamoorthy, D., 2009. Influence of process parameters for coating of nickel–phosphorous on carbon fibers. *Journal of Materials Processing Technology* 209 (6), 3022–3029.
- Kar, K.K., Rahaman, A., Agnihotri, P., Sathiyamoorthy, D., 2009. Synthesis of carbon nanotubes on the surface of carbon fiber/fabric by catalytic chemical vapor deposition and their characterization. *Fullerenes, Nanotubes and Carbon Nanostructures* 17 (3), 209–229.
- Kar, K.K., Pramanik, S., 2014. Hydroxyapatite poly (etheretherketone) nanocomposites and method of manufacturing same, U.S. Patent, Editor 2014, US Patent US8652373 B2, February 18: US.
- Keddie, J., Routh, A.F., 2010. *Fundamentals of Latex Film Formation: Processes and Properties*. Gildford: Springer Science & Business Media.
- Keddie, J.L., 1997. Film formation of latex. *Materials Science Engineering R: Reports* 21 (3), 101–170.
- Kellam, M., 1999. Aluminum-palladium alloy for initiation of electroless plating, Google Patents, US5,907,790.
- Kesmez, Ö., Çamurlu, H.E., Burunkaya, E., Arpaç, E., Cells, S., 2009. Sol–gel preparation and characterization of anti-reflective and self-cleaning SiO_2 – TiO_2 double-layer nanometric films. *Solar Energy Materials* 93 (10), 1833–1839.
- Khojasteh, D., Kazerooni, M., Salarian, S., Kamali, R., 2016. Droplet impact on superhydrophobic surfaces: A review of recent developments. *Journal of Industrial and Engineering Chemistry* 42, 1–14.
- Kılıç, F., Gül, H., Aslan, S., Alp, A., Akbulut, H., 2013. Effect of CTAB concentration in the electrolyte on the tribological properties of nanoparticle SiC reinforced Ni metal matrix composite (MMC) coatings produced by electrodeposition. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 419, 53–60.
- Kim, B.-R., 2011. VOC emissions from automotive painting and their control: A review. *Environmental Engineering Research* 16 (1), 1–9.
- Koivuluoto, H., Stenroos, C., Kylvälähti, M., *et al.*, 2017. Anti-icing behavior of thermally sprayed polymer coatings. *Journal of Thermal Spray Technology* 26 (1–2), 150–160.
- Kuang, K., Sturdivant, R., 2017. *RF and Microwave Microelectronics Packaging II*. Springer International Publishing AG. Available from: www.link.springer.com.
- Kushwaha, S., Kar, K.K., Krishnan, P.S.G., Sharma, S., 2011. Preparation and characterization of nickel coated carbon fiber reinforced polycarbonate composites. *Journal of Reinforced Plastics and Composites* 30 (14), 1185–1196.
- La Casse, R.G., Creasy W.S., 1999. Scratch-resistant anti-fog coating composition incorporating isocyanate-reactive surfactants, US Patent 5,877,254 A.
- Lee, J.A., Chen P.-S., 2005. High strength aluminum alloy for high temperature applications, Google Patents, US6,918,970.
- Liang, B., Zhang, G., Liao, H., Coddet, C., Ding, C., 2010. Structure and tribological performance of nanostructured ZrO_2 -3 mol% Y_2O_3 coatings deposited by air plasma spraying. *Journal of thermal spray technology* 19 (6), 1163–1170.
- Lin, Y., Chen, H., Wang, G., Liu, A., 2018. Recent progress in preparation and anti-icing applications of superhydrophobic coatings. *Coatings* 8 (6), 208.
- Liu, Y., Moevius, L., Xu, X., *et al.*, 2014. Pancake bouncing on superhydrophobic surfaces. *Nature Physics* 10 (7), 515.
- Ma, I.W., Sh, A., Ramesh, K., *et al.*, 2017. Anticorrosion properties of epoxy-nanochitosan nanocomposite coating. *Progress in Organic Coatings* 113, 74–81.
- Macke, A., Schultz, B., Rohatgi, P.K., 2012. Metal matrix composites offer the automotive industry an opportunity to reduce vehicle weight, improve performance. *Advanced Materials and Processes* 170, 19–23.
- Malshe, V., Waghoo, G., 2004. Chalk resistant epoxy resins. *Progress in Organic Coatings* 51 (3), 172–180.
- Manna, A., Pramanik, S., Tripathy, A., *et al.*, 2016. Design and development of an in situ synthesized layered double hydroxide structure of Fe-induced hydroxyapatite for drug carriers. *RSC Advances* 6 (30), 25549–25561.
- Marikkannu, K., Amutha, K., Kalaigann, G.P., Vasudevan, T., 2004. Studies on nickel-alumina electrocomposite coatings over mild steel substrate. In: *Proceedings of the International Symposium of Research Studenton Material Science and Engineering*.
- Marrion, A., 2004. *The Chemistry and Physics of Coatings*, second ed. Royal Society of Chemistry.
- Mason, G., 1973. Formation of films from latices a theoretical treatment. *British Polymer Journal* 5 (2), 101–108.
- Matheson, R.R., 2002. 20th-to 21st-century technological challenges in soft coatings. *Science* 297 (5583), 976–979.
- Meletis, E.I., Nie, X., Wang, F.L., Jiang, J.C., 2002. Electrolytic plasma processing for cleaning and metal-coating of steel surfaces. *Surface and Coatings Technology* 150 (2), 246–256.
- Mertaniemi, H., Laukkanen, A., Teirfolk, J.-E., Ikkala, O., Ras, R.H., 2012. Functionalized porous microparticles of nanofibrillated cellulose for biomimetic hierarchically structured superhydrophobic surfaces. *RSC Advances* 2 (7), 2882–2886.
- Miracle, D., 2005. Metal matrix composites – From science to technological significance. *Composite Science and Technology* 65 (15–16), 2526–2540.
- Moghadam, A.D., Schultz, B.F., Ferguson, J., *et al.*, 2014. Functional metal matrix composites: Self-lubricating, self-healing, and nanocomposites-an outlook. *JOM* 66 (6), 872–881.
- Moradi, A., Ataollahi, F., Sayar, K., *et al.*, 2016. Chondrogenic potential of physically treated bovine cartilage matrix derived porous scaffolds on human dermal fibroblast cells. *Journal of Biomedical Materials Research Part A* 104 (1), 245–256.
- Nair, V., Dave B.C., 2014. Anti-reflective and anti-soiling coatings with self-cleaning properties, Google Patents, US8,864,897.
- Nakajima, A., Koizumi, S.-I., Watanabe, T., Hashimoto, K., 2000. Photoinduced amphiphilic surface on polycrystalline anatase TiO_2 thin films. *Langmuir* 16 (17), 7048–7050.
- Nosonovsky, M., Bhushan, B., 2012. *Green Tribology: Biomimetics, Energy Conservation and Sustainability*. Springer.
- Nosonovsky, M., Hejazi, V., Nyong, A.E., Rohatgi, P.K., 2011. Metal matrix composites for sustainable lotus-effect surfaces. *Langmuir* 27 (23), 14419–14424.
- O'Fallon Casting Pvt. Ltd., 2019. Al/SiC Metal Matrix Composite (MMC). Available from: <https://nam03.safelinks.protection.outlook.com?url=https%3A%2F%2Fwww.ofalloncasting.com%2Fproducts%2FAl-sic-metal-matrix-composite-mmc&data=02%7C01%7CMRW-MTCP-S%40elsevier.com%7C729771de05eb44d23c5608d803018f0c%7C9274ee3f94254109a27f9b15c10675d%7C0%7C0%7C637262653379825278&data=tboMLrQF6NW8108Jzz9qr%2B0fNa4eQK0tcYJ79%2Bby4%3D&reserved=0>.
- Pardo, A., Merino, M., Arrabal, R., *et al.*, 2006a. Effect of Ce surface treatments on corrosion resistance of A3xx. x/SiCp composites in salt fog. *Surface and Coatings Technology* 200 (9), 2938–2947.
- Pardo, A., Merino, M.C., Arrabal, R., *et al.*, 2006b. Effect of La surface treatments on corrosion resistance of A3xx.x/SiCp composites in salt fog. *Applied Surface Science* 252 (8), 2794–2805.
- Paul, S., 1977. Water-borne acrylic emulsion paints. *Progress in Organic Coatings* 5 (1), 79–96.
- Pavan, C., BR, N.B., 2018. Review of ceramic coating on mild steel methods, applications and opportunities. *International Journal of Advances in Scientific Research and Engineering*. 4.
- Pramanik, S., Kar, K.K., 2011. Synthesis of carbon nanofibers on hydroxyapatite by flame deposition. *Fullerenes, Nanotubes and Carbon Nanostructures* 19 (7), 605–616.
- Pramanik, S., Kar, K.K., 2012. Functionalized poly (ether ether ketone): Improved mechanical property and acellular bioactivity. *Journal of Applied Polymer Science* 123 (2), 1100–1111.
- Pramanik, S., Cherusseri, J., Baban, N.S., Sowtharya, L., Kar, K.K., 2017. Metal matrix composites: Theory, techniques, and applications. In *Composite Materials*. Springer. pp. 369–411.
- Prasad, S., Asthana, R., 2004. Aluminum metal-matrix composites for automotive applications: Tribological considerations. *Tribology Letters* 17 (3), 445–453.
- Rahaman, A., Kar, K.K., 2011. Effect of coating time and temperature on electroless deposition of cobalt-phosphorous for the growth of carbon nanotubes on the surface of e-glass fibers/fabric. *Fullerenes, Nanotubes, and Carbon Nanostructures* 19 (5), 373–397.
- Rahaman, A., Kar, K., 2014. Carbon nanomaterials grown on E-glass fibers and their application in composite. *Composites Science and Technology* 101, 1–10.
- Rahaman, A., Patra, N., Kar, K.K., 2008. Self catalyzing behavior of kanthal wire for coating of carbon nanotubes. *Fullerenes, Nanotubes, and Carbon Nanostructures* 16 (1), 78–87.

- Rahaman, A., Kar, K.K., Chaudhary, D., 2010. Synthesis of carbon nanotubes on nickel-silica catalyst coated E-glass fiber/fabric and its nanocomposites. *International Journal of Plastics Technology* 14 (1), 65–79.
- Richard, D., Clanet, C., Quéré, D., 2002. Surface phenomena: Contact time of a bouncing drop. *Nature* 417 (6891), 811.
- RichEnergy Technology Co., Ltd., 2010. MMC Application for High Efficiency Heat Sink Available from: <https://nam03.safelinks.protection.outlook.com/?url=http%3A%2F%2Fwww.retctw.com%2Fmmc-application-for-high-efficiency-heat-sink&data=02%7C01%7CMRW-MTCP-S%40elsevier.com%7C729771de05eb44d23c5608d803018f0c%7C9274ee3f94254109a27f9fb15c10675d%7C0%7C0%7C63726265379825278&data=k2jszuAXSZqYb37lcp4KbFvssqm0UK8YrNi09Nn1W%2FM%3D&reserved=0>.
- Rocha, S., Donida, M., Marques, A., 2009. Liquid-particle surface properties on spouted bed coating and drying performance. *The Canadian Journal of Chemical Engineering* 87 (5), 695–703.
- Rohatgi, P., 1991. Cast aluminum-matrix composites for automotive applications. *JOM* 43 (4), 10–15.
- Rohatgi, P., 2014. Al-shape memory alloy self-healing metal matrix composite. *Materials Science and Engineering: A* 619, 73–76.
- Rohatgi, P., Schultz, B., 2007. Lightweight metal matrix nanocomposites – Stretching the boundaries of metals. *Material Matters* 2 (4), 16. Available from: <https://www.sigmadrich.com/technical-documents/articles/material-matters/lightweight-metal.html>.
- Rosso, M., 2006. Ceramic and metal matrix composites: Routes and properties. *Journal of Materials Processing Technology* 175 (1–3), 364–375.
- Ruhi, G., Modi, O., Sinha, A., Singh, I., 2008. Effect of sintering temperatures on corrosion and wear properties of sol-gel alumina coatings on surface pre-treated mild steel. *Corrosion Science* 50 (3), 639–649.
- Sakka, S., Kozuka, H., 2005. *Handbook of Sol-Gel Science and Technology*. 1. Sol-Gel Processing. 1. Springer Science & Business Media.
- Sathiyagnanam, A., Saravanan, C., Dhandapani, S., 2010. Effect of thermal-barrier coating plus fuel additive for reducing emission from DI diesel engine. In: *Proceedings of the World Congress on Engineering*.
- Sharma, R., Kar, K.K., 2014. Carbon nanotube coated carbon fiber based composite filaments for luminescent bulbs. *Materials Letters* 137, 150–152.
- Sharma, R., Kar, K.K., 2015a. Hierarchically structured catalyst layer for the oxygen reduction reaction fabricated by electrodeposition of platinum on carbon nanotube coated carbon fiber. *RSC Advances* 5 (82), 66518–66527.
- Sharma, R., Kar, K.K., 2015b. Particle size and crystallographic orientation controlled electrodeposition of platinum nanoparticles on carbon nanotubes. *Electrochimica Acta* 156, 199–206.
- Shirvanimoghaddam, K., Hamim, S.U., Akbari, M.K., *et al.*, 2017. Carbon fiber reinforced metal matrix composites: Fabrication processes and properties. *Composites Part A: Applied Science Manufacturing* 92, 70–96.
- Singh, B.B., Balasubramanian, M., 2009. Processing and properties of copper-coated carbon fibre reinforced aluminium alloy composites. *Journal of Materials Processing Technology* 209 (4), 2104–2110.
- Singh, S.K., Azad, P., Akhtar, M., Kar, K.K., 2018. Improved methanol detection using carbon nanotube-coated carbon fibers integrated with a split-ring resonator-based microwave sensor. *ACS Applied Nano Materials* 1 (9), 4746–4755.
- Szczygieł, B., Kołodziej, M., 2005. Composite Ni/Al₂O₃ coatings and their corrosion resistance. *Electrochimica Acta* 50 (20), 4188–4195.
- Takagi, M., Ohta, H., Imura, T., Kawamura, Y., Inoue, A., 2001. Wear properties of nanocrystalline aluminum alloys and their composites. *Scripta Materialia* 44 (8–9), 2145–2148.
- Tam, J., Palumbo, G., Erb, U., 2016. Recent advances in superhydrophobic electrodeposits. *Materials* 9 (3), 151.
- Thiémig, D., Lange, R., Bund, A., 2007. Influence of pulse plating parameters on the electrocodeposition of matrix metal nanocomposites. *Electrochimica Acta* 52 (25), 7362–7371.
- Thiruselvam, K., 2015. Thermal barrier coatings in internal combustion engine. *Journal of Chemical and Pharmaceutical Sciences* 7, 413–418.
- Thurber, C.R., Ahmad, Y.H., Calhoun, M.C., *et al.*, 2018. Metal matrix composite coatings of cupronickel embedded with nanoplatelets for improved corrosion resistant properties. *International Journal of Corrosion* 2018, 5250713.
- Torres, B., Garrido, M.A., Rico, A., *et al.*, 2010. Wear behaviour of thermal spray Al/SiCp coatings. *Wear* 268 (5), 828–836.
- Tran, T., Staat, H.J., Susarey-Arce, A., *et al.*, 2013. Droplet impact on superheated micro-structured surfaces. *Soft Matter* 9 (12), 3272–3282.
- Wallace, J.S., Ilavsky, J., 1998. Elastic modulus measurements in plasma sprayed deposits. *Journal of Thermal Spray Technology* 7 (4), 521–526.
- Wang, P., Deng, S., He, Y., Liu, C., Zhang, J., 2016. Influence of polyethylene glycol on cathode plasma electrolytic depositing Al₂O₃ anti-oxidation coatings. *Ceramics International* 42 (7), 8229–8233.
- Wang, Y., Kats, A., Juhue, D., *et al.*, 1992. Freeze-fracture studies of latex films formed in the absence and presence of surfactant. *Langmuir* 8 (5), 1435–1442.
- Wang, Z., Gao, D., 2014. Friction and wear properties of stainless steel sliding against polyetheretherketone and carbon-fiber-reinforced polyetheretherketone under natural seawater lubrication. *Materials & Design* 53, 881–887.
- Wenzel, R.N., 1936. Resistance of solid surfaces to wetting by water. *Industrial and Engineering Chemistry* 28 (8), 988–994.
- Witte, F., Feyerabend, F., Maier, P., *et al.*, 2007. Biodegradable magnesium–hydroxyapatite metal matrix composites. *Biomaterials* 28 (13), 2163–2174.
- Wu, Q., Li, W., Zhong, N., Gang, W., Haishan, W., 2013. Microstructure and wear behavior of laser cladding VC–Cr₇C₃ ceramic coating on steel substrate. *Materials & Design* 49, 10–18.
- Xu, S., Gao, X., Hu, M., *et al.*, 2014. Nanostructured WS₂–Ni composite films for improved oxidation, resistance and tribological performance. *Applied Surface Science* 288, 15–25.
- Yadav, A., De, B., Singh, S.K., Sinha, P., Kar, K.K., 2019. Facile development strategy of a single carbon-fiber-based all-solid-state flexible lithium-ion battery for wearable electronics. *ACS Applied Materials & Interfaces* 11 (8), 7974–7980.
- Yamini Sarada, B., Agarwal, S., Kar, K.K., 2009. A simple method for controlled growth of carbon nanocoils on metallic wire by chemical vapor deposition. *Nanoscience and Nanotechnology Letters* 1 (3), 213–217.
- Yih, P., Chung, D.L., 1997. Titanium diboride copper-matrix composites. *Journal of Materials Science* 32 (7), 1703–1709.
- Young, T., 1805. III. An essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society of London* 95, 65–87.
- Zhai, Y., North, T., Serrato-Rodriguez, J., 1997. Transient liquid-phase bonding of alumina and metal matrix composite base materials. *Journal of Materials Science* 32 (6), 1393–1397.
- Zhang, P., Li, G., 2016. Advances in healing-on-demand polymers and polymer composites. *Progress in Polymer Science* 57, 32–63.
- Zhong, X., Zhenmin, W., Fengying, Z., *et al.*, 1982. Double layer ion metallic cementation. *Transactions of Materials and Heat Treatment* 1, 6.
- Zhou, H.-B., Wang, J.-L., Jiang, W., *et al.*, 2016. Electrophobic interaction induced impurity clustering in metals. *Acta Materialia* 119, 1–8.
- Zimmerman, A., Palumbo, G., Aust, K., Erb, U., 2002. Mechanical properties of nickel silicon carbide nanocomposites. *Materials Science Engineering: A* 328 (1–2), 137–146.

Biocompatibility of Metal Matrix Composites Used for Biomedical Applications

Somasundaram Prasad, Santhosh Suresh, Vaishnavi Ratheesh, and Raymond Wong, National University Centre for Oral Health, Singapore

Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

The longevity of an implant biomaterial depends on the anchorage and integration between the implant and the living bone (Albrektsson *et al.*, 2003). There are various factors which determine the success of an implanted biomaterial, namely the form and structural characterization, stability, mechanical-loading, material property, location of the implanted site and host response (Legeros and Craig, 1993; Prasad *et al.*, 2019a). The key outcome is to finally derive a matrix which matches the bone in composition, structure and properties (Puleo and Nanci, 1999). Biocompatibility and mechanical strength are the most important pre-requisite characteristics of any implanted biomaterial to be employed for biomedical, orthopedic and dental applications (Gotman, 1997; Gasser *et al.*, 2000; Niinomi, 2008; Marti, 2000; Prasad *et al.*, 2019b). The host response induced by the implanted material and the degradation of the material within the body are the two major factors which determine the biocompatibility. Biocompatibility is fulfilled when there is no foreign body reaction within the tissue caused by the implanted biomaterial. The biomaterial should be non-toxic and should not elicit any allergic or negative inflammatory reactions to the host tissues (Morais *et al.*, 2010). However, the biocompatibility of a material is dependent on the physiological interaction between the host cells/tissues and the implants. If there is a derangement in the interaction between the host cells/tissues and the implanted biomaterial, the immediate reaction is thrombosis and fibrous encapsulation leading to the failure of the implanted material (Williams, 1987).

A biomaterial is said to possess adequate mechanical characteristics in order to elucidate the functionality of the implants mainly in the load bearing orthopedic applications. Metallic biomaterials are preferred to polymers because of their high mechanical strength and reasonable corrosion resistance. The metallic biomaterial should have good tensile strength, young's modulus, wear, corrosion resistance, bioactivity and biocompatibility (Prasad *et al.*, 2017). There are various biodegradable and non-degradable metallic biomaterials available as implant material for both load bearing and non-load bearing applications. Stainless steel (316L), cobalt chromium (Co-Cr) alloys, titanium (Ti)/titanium alloys and magnesium alloys have been used as implant materials (Geetha *et al.*, 2009; Paital and Dahotre, 2009) (Table 1).

In case of a trauma surgery, stainless steel (316L) has been proven to be a good metallic implant (Navarro *et al.*, 2008). It exhibits good mechanical strength, ductility, elastic property, easily manufacturability and is available at low cost. However, the drawbacks of stainless steel are low resistance to corrosion and less biocompatibility due to the presence of nickel content causing allergic reactions (Gotman, 1997), hereby limiting their usage for short-term temporary implant surgeries (Gasser *et al.*, 2000). Co-Cr metallic alloys have replaced stainless steel as a permanent implant material due to its excellent mechanical property and high corrosion resistance (Marti, 2000). Co-Cr combined with molybdenum (Mo) shows excellent corrosion resistance and high fatigue (Marti, 2000; Navarro *et al.*, 2008; Bensmann, 1999; Disegi and Eschbach, 2000; Ha, 2008; Heuberger, 2009; Marti *et al.*, 2000). Nevertheless, the main drawback of these materials is biocompatibility and allergic reactions (Breme *et al.*, 2002; Christensen *et al.*, 2000; Keegan *et al.*, 2008). Titanium and titanium alloys have excellent biocompatibility, mechanical strength, and good elasticity and cause no allergic reaction. Besides its excellent properties and its wide applicability, the drawbacks of these alloys are non-degradability and stress shielding effects. Apparently, there is a need for a second surgical procedure to remove the implanted titanium alloys (Daley *et al.*, 2004; Disegi, 1993; Shapira *et al.*, 2009; Thompson and Puleo, 1996; Thomsen *et al.*, 1997). The Young's modulus of titanium (110–120 GPa) does not match with that of the natural bone (10–20 GPa) thereby causing stress shielding at the implanted bone site (Heary *et al.*, 2017). Magnesium alloys are able to overcome the drawbacks of titanium alloys. Magnesium alloys are biodegradable, their Young's modulus (40–45 GPa) is a near match with the natural bone, thereby eliminating the stress shielding effect and avoiding the need for a second surgical procedure to remove the implanted material. Interestingly, magnesium alloys are biocompatible and are capable of undergoing complete degradation. On the other hand, zinc and iron alloys are also biodegradable and are successfully employed for various biomedical applications. This article will attempt to provide an in-depth discussion about the biocompatibility of various metal matrix composites used for biomedical applications in both load bearing and non-loading bearing scenarios (Tables 2 and 3).

Biomaterial and Cellular Interaction

Any material is said to be biocompatible when it does not disturb the normal body functions. Biocompatibility of any implant material depends on factors like size, shape, surface and composition of the material (Tang *et al.*, 2017). The implanted biomaterial should not cause any allergic reactions, thrombus formation, and should not alter the cellular elements in the blood and electrolytes. The implanted material should be within the body until the expected outcome of regeneration of the bone or tissue or an organ has

Table 1 Comparison between permanent metallic materials and biodegradable metals

Items	Permanent metallic materials	Biodegradable metals
Mechanical property	Stable over time	Degraded with time, and should match the tissue recovery process
Ion release	Unwanted, try to avoid	The released metal ions should be acceptable by the host locally and all over the body
Interaction with the surrounding tissue	Bio-inert	Bio-active
Application fields	Ubiquitous	Special applications

Note: Geetha, M., *et al.*, 2009. Ti based biomaterials, the ultimate choice for orthopaedic implants – A review. *Progress in Materials Science* 54 (3), 397–425. Paital, S.R., Dahotre, N. B., 2009. Calcium phosphate coatings for bio-implant applications: Materials, performance factors, and methodologies. *Materials Science and Engineering: R: Reports* 66 (1–3), 1–70.

Table 2 Comparison of the physical and mechanical properties of various biomaterials and natural bone

Material	Density (g/cm ³)	Elastic modulus (GPa)	Yield strength (MPa)	Fracture toughness (MPa m ^{1/2})	References
Human Cortical bone	1.80–2.10	3–20	130–193	3–6	Davis <i>et al.</i> (1998), Kuwahara <i>et al.</i> (2000)
Mg	1.74–2.00	41–45	65–100	15–40	Kuwahara <i>et al.</i> (2000)
AZ91	1.81	45	160	N/A	Williams (2006)
WE43	1.84	44	170	N/A	Witte <i>et al.</i> (2008)
Mg–6Zn	N/A	42.3	169.5	N/A	Li and Zheng (2013)
Mg–1Ca–Zn	N/A	45.3	67	N/A	Poinern <i>et al.</i> (2012)
Ti alloy	4.40–4.50	110–117	758–1117	55–115	Kuwahara <i>et al.</i> (2000), Gu <i>et al.</i> (2009)
Ti6Al4V	4.40	115	900	N/A	Bommala <i>et al.</i> (2018)
Co–Cr alloy	8.30–9.20	230	450–1000	N/A	Kuwahara <i>et al.</i> (2000)
XLPE	0.47–1.26	0.005–0.69	20	N/A	Kuwahara <i>et al.</i> (2000)
Synthetic-HA	3.10	73–117	600	0.7	Chen <i>et al.</i> (2010)

Abbreviations: GPa, GigaPascal, MPa, MegaPascal.

been attained. If the implanted material degrades faster than the regenerating tissue, the material will lose its mechanical and physical properties that would potentiate it to withstand the forces and the chemical changes acting on it. In reality, there is no one single material which remains intact throughout the implantation period without undergoing any characteristic changes. The pace at which the material degrades can be altered by the addition of an alloying element to it. The degradation products and ions released from the material will further trigger changes in the surrounding biological environment of the implant. Immediately after the implantation process, there is an initial inflammatory response elicited by the injured blood vessels. This mostly leads to blood clot formation, unlike in some cases it results in thrombosis (Velnar *et al.*, 2016). There is an event of changes in the plasma proteins and emigration of leukocytes to the implanted area. The most common cells found around the implant site immediately after the implantation are the monocytes and lymphocytes which are more pronounced in chronic inflammatory phase. If the chronic inflammation does not subside within 3 weeks of implantation, there is a high chance of persisting infection that can eventually lead to implant failure. Besides, the surgical procedure adopted during implant placement also plays a crucial role in the healing process. If injury to the tissues and vessels occurs during the implantation procedure, it leads to increased amount of granulation tissue formation surrounding the implant area after 3–5 days post-implantation (Pippi, 2017). The ultimate success or failure of an implant material depends on the initial interface between the implant and the surrounding bone. An indicator for poor biocompatibility is the formation of fibrous tissue between the implant and the surrounding bone (Prasadh *et al.*, 2020; Prasadh and Wong, 2018).

The degradation of implant material around the implant activates the phagocytes and the giant macrophages leading to the release of inflammatory cytokines causing inflammatory changes like fibrosis, osteolysis and porosis in the bone (Bitar and Parvizi, 2015). This further leads to the formation of synovial-like interface between the bone and the implant leading to the formation of granulation tissues leading to implant loosening. The degradation rate of the implanted material further affects the inflammatory reactions both near and away from the implant area. The increased degradation of the implant material further increases concentration of the metallic ions around the implanted area. These metallic ions cause changes in the biological cellular environment and alter the electric current affecting the cellular metabolism (Guillory *et al.*, 2019, 2016). The released ions from the degraded implants may cause localized to systemic effects within the body. There could be acute pain, swellings, tenderness and localized discoloration of the surrounding tissues. The increased ion concentration if not excreted completely would lead to toxic effects in the vital organs like kidney and liver causing metallosis (Guillory *et al.*, 2019; Bowen *et al.*, 2016). Metals like cobalt, chromium and nickel causes metallosis by causing destruction of hard and soft tissues surrounding the implant (Hong *et al.*, 2016; Jin *et al.*, 2018; Morin *et al.*, 2017). The metal ion by itself does not cause immune response. It is shown that the released metal ions from the materials combine with protein biomolecules surrounding the implant area, thereby inducing the inflammatory

Table 3 Metallic non-resorbable materials advantages, disadvantages and applications

<i>Materials</i>	<i>Advantages</i>	<i>Disadvantages</i>	<i>Applications</i>
<i>316L Stainless steel</i>	Easily available and low cost Excellent fabrication properties Accepted biocompatibility and toughness	High modulus Poor corrosion resistance Poor wear resistance Allergic reaction in surrounding tissue Stress shielding effect	Bone Plates, Bone screws and pins, Wires etc.
<i>Co-Cr alloys</i>	Superior in terms of resistance to corrosion, fatigue and wear High strength Long term biocompatibility	Expensive Quite difficult to machine Stress shielding effect High Modulus Biological toxicity due to Co, Cr and Ni ions release	Shorter term implants-Bone plates and wires, Total hip replacements (THR)-Stem or hard-on-hard bearing system
<i>Ti alloys</i>	Excellent resistance to corrosion Lower Modulus Stronger than stainless steels Light weight Biocompatible	Poor wear resistance Poor bending ductility Expensive	Fracture Fixation plates, Fasteners, nails, rods, screws and wires, Femoral hip stems, Total Joint Replacement (TJR) arthroplasty-hips and knees

reactions causing toxicity. The major factor to be considered in this mechanism is how readily the ion particles combine with the protein biomolecules. For metals like Ti, Zr, Ne, Mg and tantalum when the ions are released, they react immediately with available OH^- groups and anions to form ion oxides and salt crystals in the body. So, the ions from these materials are not free to combine with the protein biomolecules to precipitate the inflammatory adverse reaction causing toxicity. Whereas ions of cobalt, chromium and nickel do not combine with anions or any other hydroxyl groups and remain free for long time and gets attached with protein biomolecules to cause inflammatory adverse reaction and toxicity ([Table 4](#)).

Metals Used for Biomedical Applications

Stainless Steel

Stainless steel can be easily cast into different shapes and sizes and was indeed the first material to be used to fabricate artificial bone. Hatfield introduced 18/8 stainless steel in 1920 which was able to overcome the limitations such as lower corrosion resistance and mechanical strength ([Hatfield, 1931](#)). The rate of metal sensitivity and incidence of the implant failure were lesser than other stainless steel grades and with fewer post-surgical complications. The carbon content of the stainless steel (18/8) was reduced to limit the formation of chromium carbides causing toxic reaction (allergic). The chromium content above 12 wt% with Ni and Mo was used to reduce the carbon content ([Eliaz and Metoki, 2017](#)). Although nickel helps in increasing corrosion resistance, it also reduces biocompatibility ([Rushing et al., 2007](#)). Nickel causes allergic reaction when implanted in the body. So, the SS used for biomedical applications are called as conventional SS to avoid Ni. Nitrogen is used along with the alloying elements to reduce the allergic reaction caused by nickel. The stainless steel without nickel are biocompatible and used for load bearing application and as arterial stent ([Ducheyne and Kohn, 1998](#)). The 316L stainless steel has low carbon content less than 0.03% and is widely used in bone fracture plates, screws, and nails in surgical practice for temporary purpose. The plates should be removed after the healing of the fracture. The 316L SS corrodes inside the body at highly stressed oxygen depleted environment. The lower carbon content helps to increase the corrosion resistant and ASTM has recommended 316L as a principal alloy for implant fabrication ([Driscoll, 2009](#)).

Cobalt Chromium Alloys

Compared to Ti Alloys, Co-based implants have higher wear resistance. In cases of hip joint replacements, where there is an excessive chance of wear between the femoral head and the bone or plate, cobalt based alloys are well suited ([Alvarado et al., 2003](#)). Co- based

Table 4 Summary of the pathophysiology and toxicology of various alloying elements

Element	Blood serum level	Daily allowance	Pathophysiology	Toxicology
<i>Essential Elements</i>				
Mg	17.7–25.8 mg/L	700 mg	Activator of many enzymes; co-regulator of protein synthesis and muscle contraction; stabilizer of DNA and RNA	Excessive Mg leads to nausea
Ca	36.8–39.8 mg/L	800 mg	More than 99% have structural functions in the skeleton; the solution Ca has signaling functions, including muscle contraction, blood clotting, cell function, etc.	Inhibit the intestinal absorption of other essential minerals
Fe	5000–17,600 mg/L	10–20 mg	Component of several metalloproteins; crucial in vital biochemical activities, i.e., oxygen sensing and transport	Iron toxicity gives rise to lesions in the gastrointestinal tract, shock and liver damage
<i>Essential Trace Elements</i>				
Zn	0.8–1.14 mg/L	15 mg	Trace element; appears in all enzyme classes; most Zn appears in muscle	Neurotoxic and hinders bone development at higher concentrations
Cu	4.51–8.32 mg/L	1–3 mg	Cu plays a vital role in the immune system; has beneficial effects on endothelial cell proliferation and has been reported to enhance antibacterial properties	Excessive Cu (> 1 mg/day) can cause neurodegenerative diseases, including Alzheimer's, Menkes and Wilson's diseases
Mn	< 0.0008 mg/L	4 mg	Activator of enzymes; Mn deficiency is related to osteoporosis, diabetes mellitus, and atherosclerosis	Excessive Mn results in neurotoxicity
<i>Other Elements</i>				
Sr	0.17 mg/L	2 mg	99% is located in bone; shows dose dependent metabolic effects on bone; low doses stimulate new bone formation	High doses induce skeletal abnormalities
Li	0.002–0.004 mg/L	0.2–0.6 mg	Used in the treatment of manic depressive psychoses	Plasma concentrations of 2 mM are associated with reduced kidney function and neurotoxicity, 4 mM may be fatal
Al	0.0021–0.0048 mg/L	–	–	Primarily accumulates in the bone and nervous systems; implicated in the pathogenesis of Alzheimer's disease; can cause muscle fiber damage; decreases osteoblast viability

Note: Witte, F., *et al.*, 2008. Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State and Materials Science* 12 (5–6), 63–72. Gu, X.-N., Zheng, Y.-F., 2010. A review on magnesium alloys as biodegradable materials. *Frontiers of Materials Science in China* 4 (2), 111–115. Mostaed, E., *et al.*, 2016. Novel Zn-based alloys for biodegradable stent applications: Design, development and in vitro degradation. *Journal of the Mechanical Behavior of Biomedical Materials* 60, 581–602. Zheng, Y., Gu, X., Witte, F., 2014. Biodegradable metals. *Materials Science and Engineering: R: Reports* 77, 1–34.

alloys are used for orthopedic prosthesis due to their excellent corrosion resistance in chloride environment which could be attributed by the alloying elements added to it. They form a protective Co_2O_3 passivating layer thereby preventing the wear and corrosion. The most commonly use cobalt based alloy is Co-Cr-Mo due to its high strength and high ductility. With the addition of Nickel, the alloy CoNiCrMo also called as MP35N contains 35% Co and Ni, thereby demonstrating excellent corrosion resistance and high mechanical strength compared to cast Co-Cr alloy (Aherwar *et al.*, 2016). However, nickel is potentially toxic and use of CoCr-Ni-Mo is not recommended for applications concerning the biocompatibility. The Co-Cr alloy has high elastic modulus compared to Ti or Ti Alloys (Aherwar *et al.*, 2016; Li *et al.*, 2004). But Co-Cr has high elastic modulus compared to bone which leads to greater stress shielding effect when compared to Ti, Ti alloys or Mg Alloys (Nayak *et al.*, 2016). Compared to titanium or magnesium alloys, the osteointegration capacity and biocompatibility of Co-Cr is reduced. Li *et al.* (2014). Hence, in a clinical scenario that presents with a need for direct contact of the implant material and bone, Ti or Mg can be used (screws and pins). Co-Cr can be used in cases where there would be no interface with the bone (Rods in spinal fixation). In situations where Ti and Co-Cr Alloys are in close contact, there is shredding at the site of contact due to frictional load. The tissue near these materials experiences metallosis (Nayak *et al.*, 2016).

Titanium Matrix Composites

Titanium and its alloys are mainly used as implants in the field of orthopedics and dentistry. Besides implants, these biomaterials are also being used as surgical guides and tools. The main reasons for them to be an ideal material for biomedical applications can be attributed to their striking features such as biocompatibility, high strength, and good corrosion resistance (Faria *et al.*, 2008). Compared to stainless steel, titanium has a higher strength to weight ratio, which means that titanium is stronger but lighter.

Table 5 Elastic modulus of the cortical bone, commercially pure titanium (CP-Ti) and Ti6Al4V alloy

Material	Specification	Elastic modulus (GPa)
Bone	–	≤ 30
CP-Ti	ASTM F67 Grade 1	103–107
CP-Ti	ASTM F67 Grade 2	103–107
CP-Ti	ASTM F67 Grade 3	103–107
CP-Ti	ASTM F67 Grade 4	103–107
Ti6Al4V	ASTM F136 Grade 5	114–120

Abbreviation: GPa, GigaPascal.

Note: ASTM F136, 2013. Standard Specification for Wrought Titanium-6Aluminum-4Vanadium ELI (Extra Low Interstitial) Alloy for Surgical Implant Applications (UNS R56401). ASTM F, 1981. Standard Specification for Unalloyed Titanium for Surgical Implant Applications. American Society for Testing and Materials, Philadelphia, PA.

Possessing these favorable properties, titanium and its alloy's application are not just limited to the biomedical field, but have also gained significance in the aerospace, automotive, and marine industries.

When to be used in various parts of the body, it is important to understand the site and purpose of the implants. For example, as a load-bearing implant, hip or knee implant would require a stiffer biomaterial as compared to a heart stent. Besides, hip and knee have movable joints which would subject the implants to increased wear and tear. For these reasons, researchers are constantly focusing on developing new alloying materials to enhance their properties in terms of biocompatibility, stiffness, and corrosion resistance. One example is the replacement of commercially used pure titanium (CP-Ti) to Ti6Al4V (Ti64) to Ti-Nb-Zr (Silva *et al.*, 2004). The American Society for Testing and Materials (ASTM) has categorized these materials into different grades, some of which are used as surgical implants (ASTM F136, 2013; ASTM F, 1981). Others have also been researched for coating the metals to improved osseointegration (Morin *et al.*, 2017; Subramani *et al.*, 2016; Wong *et al.*, 2011; Zhang *et al.*, 2018a).

Despite medical acceptance, the stiffness of some of these materials is too high as compared to the human bone which causes bone stress-shielding. Moreover, the toxicity of vanadium, the alloying element, has raised concerns. Thus, it is in the interest of researchers to develop the ideal titanium-based biomaterial that are biocompatible and exhibit good mechanical properties and good corrosion resistance properties.

Titanium Matrix Composites (TMCs) are materials that consist of titanium or titanium alloys as the base material while the reinforcement can be another material like metal, ceramic or an organic compound (Table 5). TMCs are constantly developed for biomedical applications to reduce Young's modulus, enhance osseointegration and biocompatibility. Thus, it is important that materials used to form the TMCs are biocompatible. Niobium pentoxide (Nb_2O_5) is biocompatible and have been used to coat titanium alloy using a sol-gel technique that greatly improves its biocompatibility, bioactivity and corrosion resistance. In a study to improve its load-bearing strength and excellent biocompatibility, Li *et al.* fabricated a Ti-Nb $_2$ O $_5$ composite by using CP-Ti powder and reinforcing it with 2%, 3% or 4% Nb $_2$ O $_5$ particulates using a cold press (300 MPa) and sintering (1000°C) method (Moghaddam *et al.*, 2016). The biocompatibility assay showed that the osteoblast-like SaOS2 cells exhibited similar cell proliferation and variability to CP-Ti, suggesting that Ti-Nb $_2$ O $_5$ is not toxic and is biocompatible.

Diamond (D) was studied previously as a coating material for orthopedic implant materials due to its high hardness and low coefficient of friction, thus providing high wear resistance. Coated diamond films on titanium alloy implant showed that they are biocompatible and also promote osteogenesis while displaying high resistance to bacterial colonization and bioactivity at the molecular level. Using powder metallurgy, Guimaraes *et al.* combined CP-Ti powder with 2%, 5% or 10% (wt%) of diamond powder and compacted using a uniaxial pressing (100 MPa) and subsequently sintered (1250°C) the green part (Guimaraes *et al.*, 2017). Though the Ti-D composite exhibited increased stiffness, Ti-2D (2% D) had the best of physical and mechanical properties with an increase in porosity, which is favorable to osseointegration. In comparison to CP-Ti, Ti-2D was also biocompatible with better cell adhesion and proliferation of VERO cells.

Calcium phosphate (CaP) is a natural bone mineral. CaP is among the most widely used bio ceramics with excellent bio resorption and compatibility specific to enhance bone repair (Eliaz and Metoki, 2017). Most load-bearing implants are made of titanium and its alloys while some include the replacement of joints. Materials for such purposes are subjected to wear, resulting in the release of metal ions in the system. In 2016, Bandyopadhyay *et al.* fabricated a matrix of Ti-CaP and Ti64-CaP using laser-based additive manufacturing known as Laser Engineered Net Shaping (LENS) (Bandyopadhyay *et al.*, 2016). For the articulation of a load-bearing implant, they reported that both titanium matrix composite exhibited reduced wear rate while reporting an increase in strength and hardness.

Hydroxyapatite (HA) is an inorganic compound that is widely studied due to its biological importance to human bones and teeth. It also makes up 50% (vol%) of the human bones. Thus, HA is a biocompatible material. As HA stimulates bone ingrowth, HA-coated implants have enhanced osseointegration. One of the main concerns of HA-coated titanium is the reduced biocompatibility due to HA decomposition at high temperature (1400–1450°C) during the adhesion process like conventional pressing and sintering (Daugaard *et al.*, 2010). Other concerns include the detachment of the HA coating that may compromise osseointegration and subsequent implant loosening while detached particles may cause adverse effects on the surrounding tissue. Sintering Ti-HA powder at 800°C was able to produce a composite that was simple, cost-effective and biocompatible when assayed

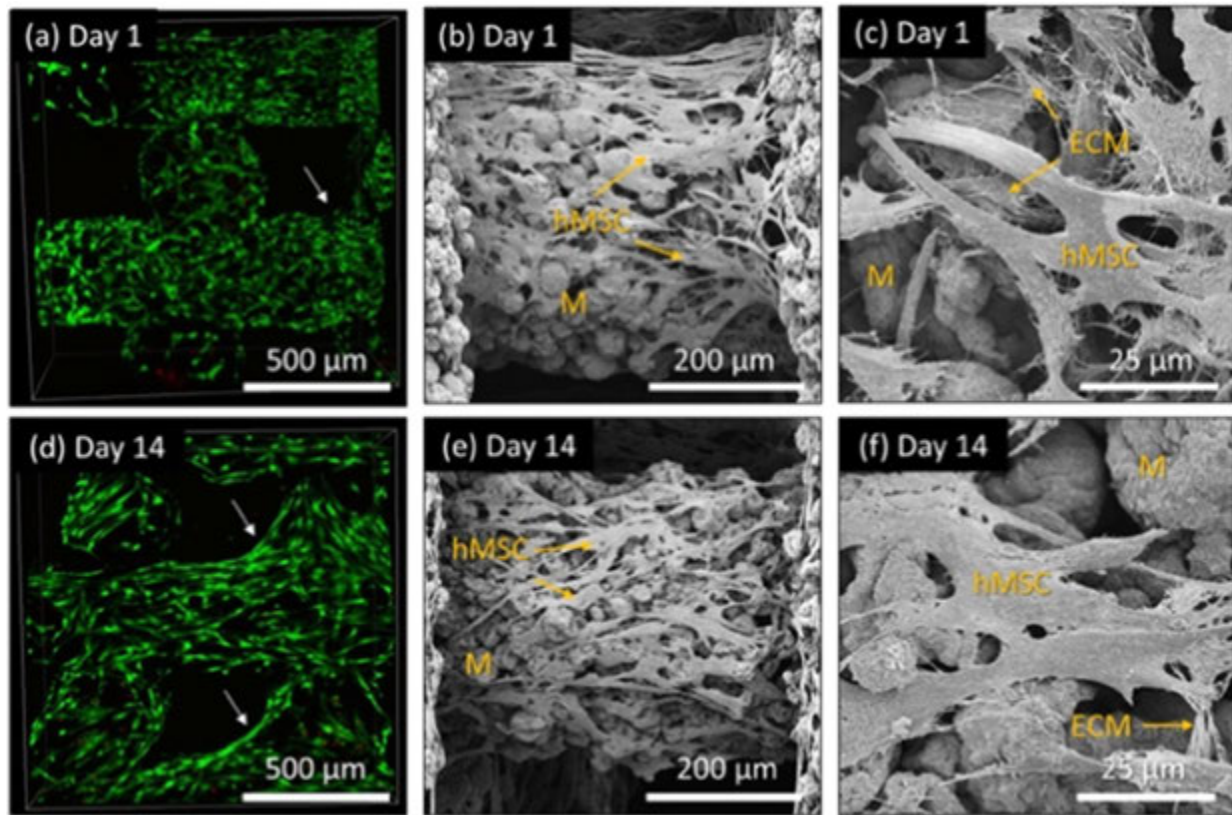


Fig. 1 (a, d) Fluorescent scanning confocal reconstructed projections of live (green) and dead (red) stained adult human mesenchymal stem cells (hMSCs) with arrows indicating expansion of the cells into the corners of the 3DP channels at Day 14; and (b-c, e-f) low and high magnification SEM images of hMSCs on metallic (M) NiTi-6.7Nb micro-trusses after Day 1 and Day 14. Evidence of extracellular matrix (ECM) is present. Reproduced from Taylor, S.L., *et al.*, 2018. NiTi-Nb micro-trusses fabricated via extrusion-based 3D-printing of powders and transient-liquid-phase sintering. *Acta Biomaterialia* 76, 359–370.

with VERO or NIH3T3 cells (Comín *et al.*, 2017). The application of ceramics like ZrO_2 is seen to have very low wear rates and negligible ion release due to their low friction coefficient. These properties are especially important for load-bearing implants, such as implants at joints. As such, Zhang *et al.* developed a novel titanium composite by introducing ZrO_2 into Ti-24Nb-4Zr-8Sn (Ti2448) via the spark plasma sintering system for 10 min at 1150°C (Zhang *et al.*, 2018b). The resultant composite, Ti2448- ZrO_2 showed improved mechanical strength and corrosion resistance thus suggesting better biocompatibility than Ti2448.

Nitinol contains nickel and titanium that is biocompatible, and its attractive properties can be used in biomedical applications such as stents, dental devices, bone implants or actuators. In a study in 2018, Taylor *et al.* studied the NiTi-Nb composite with different percentages of Nb (0, 1.5, 3.1, 6.7 at%) (Taylor *et al.*, 2018). NiTi-6.7Nb had porosities of ~75%, which is similar to trabecular bone porosity. In addition, human mesenchymal stem cells (hMSC) exhibited viability, proliferation, and extracellular matrix deposition over 14 days in culture (Fig. 1).

Magnesium (Mg) is an abundant mineral in the body and is also naturally contained in many foods. Being a biocompatible element, Mg has also been studied as temporary implant material due to its biodegradable property. Mg-based alloys are investigated to fabricate implants to enhance its mechanical and biological properties. When Mg is introduced into Ti by powder metallurgy and spark plasma sintering, it has a lower elastic modulus. Upon implantation or in vitro simulated body fluid, Mg degrades over time, decreasing the elastic modulus further while inducing the formation of a calcium phosphatase layer (Liu *et al.*, 2015a). The bioactivity also improved as pores formed on the surface for cell attachment. Ti-35.3Nb-7.3Zr-5.7Ta (TNZT), a biocompatible titanium alloy, was used as a base material. It was reinforced with Fe (0–2 wt%) and Si (0–1 wt%) by electric arc melting (1400°C) and was subsequently forged. The final composite, TNZT-Fe-Si displayed lower elastic modulus of 65–85 GPa compared with Ti6Al4V (~115 GPa), but higher than TNZT (55 GPa) and cortical bone (10–30 GPa). Furthermore, MG63 cells cultured on the composites showed higher proliferation and collagen production than standard Ti6Al4V alloy (Kopova *et al.*, 2016).

Carbon nanotubes (CNT) have also been studied for their biocompatibility previously (Schrand *et al.*, 2007; Shim *et al.*, 2002; Smart *et al.*, 2006). To relieve the stress shielding effect for conventional bone implants, CNT was added in CP-Ti at 5 wt% and 10 wt%. The Ti-CNT exhibited an increased nano-hardness and elastic modulus as compared to CP-Ti. Moreover, the composite was biocompatible when assessed using 2 different cell lines; SAOS and human aortic smooth muscle cells (hASMC), on the DNA

Table 6 Common biomedical zinc alloys

Family	Representative alloys and alloying elements (wt%)	Main phases
Zn-Mg	Zn-0.15Mg	α -Zn, Mg ₂ Zn ₁₁
	Zn-0.5Mg	α -Zn, Mg ₂ Zn ₁₁
	Zn-1Mg, ZnMg1	α -Zn, Mg ₂ Zn ₁₁
	Zn-1.2Mg	α -Zn, Mg ₂ Zn ₁₁
	Zn-1.5Mg, ZnMg1.5	α -Zn, Mg ₂ Zn ₁₁
	Zn-3Mg, ZnMg3	α -Zn, Mg ₂ Zn ₁₁
	Zn-1.5Mg-0.1Ca	α -Zn, Mg ₂ Zn ₁₁ , CaZn ₁₃
	Zn-1Mg-0.5Ca	α -Zn, Mg ₂ Zn ₁₁ , CaZn ₁₃
	Zn-1Mg-1Ca	α -Zn, Mg ₂ Zn ₁₁ , CaZn ₁₃
	Zn-1Mg-0.1Sr	Zn, MgZn ₂ , SrZn ₁₃
	Zn-1Mg-0.5Sr	Zn, MgZn ₂ , SrZn ₁₃
	Zn-1.5Mg-0.1Sr	α -Zn, Mg ₂ Zn ₁₁ , SrZn ₁₃
	Zn-1Mg-1Sr	α -Zn, Mg ₂ Zn ₁₁ , SrZn ₁₃
	Zn-1Mg-0.1Mn	Zn, MgZn ₂
	Zn-1.5Mg-0.1Mn	Zn, MgZn ₂
Zn-Ca	Zn-1Ca	α -Zn, CaZn ₁₃
	Zn-1Ca-1Sr	α -Zn, CaZn ₁₃ , SrZn ₁₃
Zn-Sr	Zn-1Sr	α -Zn, SrZn ₁₃
Zn-Al	Zn-0.5Al	Zn, Al
	Zn-1Al	Zn, Al
	Zn-3Al	Zn, Al
	Zn-5Al	Zn, Al
	ZnAl ₄ Cu ₁	Zn, Al
	ZA0.1Mg	α -Zn, Mg ₂ (Zn,Al) ₁₁
	ZA0.3Mg	α -Zn, Mg ₂ (Zn,Al) ₁₁
	ZA0.5Mg/Zn – 0.5Al – 0.5Mg	α -Zn, Mg ₂ (Zn,Al) ₁₁
	Zn-0.5Al-0.5Mg-0.1Bi	Zn, Mg ₂ (Zn,Al) ₁₁ , Mg ₃ Bi ₂
	Zn-0.5Al-0.5Mg-0.3Bi	Zn, Mg ₂ (Zn,Al) ₁₁ , Mg ₃ Bi ₂
	Zn-0.5Al-0.5Mg-0.5Bi	Zn, Mg ₂ (Zn,Al) ₁₁ , Mg ₃ Bi ₂
	3.5-0.5Al, 0.75-1.25Cu, 0.03-0.08Mg	Zn, Al
	3.5-4.3Al, 2.5-3.2Cu, 0.03-0.06Mg	Zn, Al
Zn-Cu	Zn-1Cu	η -Zn, ϵ -CuZn ₅
	Zn-2Cu	η -Zn, ϵ -CuZn ₅
	Zn-3Cu	η -Zn, ϵ -CuZn ₅
	Zn-4Cu	η -Zn, ϵ -CuZn ₅
	Zn-3Cu-0.1Mg	Zn, CuZn ₅ , Mg ₂ Zn ₁₁
	Zn-3Cu-0.5Mg	Zn, CuZn ₅ , Mg ₂ Zn ₁₁
	Zn-3Cu-1Mg	Zn, CuZn ₅ , Mg ₂ Zn ₁₁
Zn-Li	Zn-2Li	Zn, α -LiZn ₄
	Zn-4Li	Zn, α -LiZn ₄
	Zn-6Li	Zn, α -LiZn ₄
	Zn-Li	Zn, α -LiZn ₄
Zn-Ag	Zn-2.5Ag	η -Zn, ϵ -AgZn ₃
	Zn-5Ag	η -Zn, ϵ -AgZn ₃
	Zn-7Ag	η -Zn, ϵ -AgZn ₃

Note: Venezuela, J., Dargusch, M., 2019. The influence of alloying and fabrication techniques on the mechanical properties, biodegradability and biocompatibility of zinc: A comprehensive review. *Acta Biomaterialia* 87, 1–40.

damage and metabolic activity (Pavón *et al.*, 2019). Poly (methyl methacrylate) (PMMA) is biocompatible and has been widely used as medical devices, mainly known for contact lenses. Avolio *et al.* developed a new biomaterial by embedding CP-Ti nanoparticles as fillers in PMMA by solvent casting for tissue engineering purposes. Mechanical studies showed that nano fillers at 1 wt% was ideal. The composite was not toxic and did not affect the cell viability nor proliferation of the human mesenchymal stem cells (hMSC) (Avolio *et al.*, 2016).

Biodegradable Materials

Zinc Alloys

Zinc is a trace element, a significant catalyst for many enzymes, to maintain the structure and function of proteins and stabilizing the protein domains (Coleman, 1992). Most tissues are tolerant to zinc ions and they are being used as stents for bioresorbable metallic stents (Bowen *et al.*, 2016). The corrosion of zinc is influenced by the surrounding pH levels and anodic dissolution and cathodic reduction of dissolved oxygen (Bowen *et al.*, 2016). Zinc chloride and zinc oxide participates in the corrosion process at a pH of 7.3 (Bowen *et al.*, 2016). Zinc combined with Mg plays a significant role in corrosion rate, since it's not affected by the hydrogen gas evolution. Zinc is used as stents for arteries up to 6 months in rats showed no inflammatory response or thromboses. The stents showed tissue integration and partial degradation. Zinc along with magnesium is currently researched for plates and screws for fracture fixations. Zinc addition to magnesium influence the corrosion rate and mechanical property of the alloy (Heiden *et al.*, 2015). (Fig. 2).

Zinc based materials are studied for their application in cardiovascular and orthopedic applications (Table 6) (Fig. 3). The absorbable zinc materials when implanted in the body releases Zn^{2+} . The released Zn^{2+} comes in direct contact with the cells and tissues showing cellular and molecular responses. Cytotoxicity evaluation of biodegradable Zn-3Mg alloy toward normal human osteoblast cells and the cytotoxicity response of the osteoblast cells to 0.75 mg/ml Zn concentration was studied by Murni *et al.* (2015). The MC3T3 osteoblast cells did not cause any cytotoxicity. 153.8 μ M Zn concentration increased cell viability and showed no signs of cytotoxicity on pig pulmonary endothelial cells whereas increasing the concentration to 153.8 μ M inhibited cell viability and caused cell death (Murni *et al.*, 2015). Krones *et al.* (2005) showed that the concentration of Zn^{2+} from 80 to 120 μ M on human coronary artery endothelial cells showed decreased cell viability whereas concentrations below 80 μ M showed good cell viability. The morphology of the cells was affected by increased concentration. The cells were rounded and apoptosis of cells were found whereas less concentration of Zn showed well-formed flattened spindle morphology (Krones *et al.*, 2005).

Zn increased the proliferation, cell differentiation and osteogenic gene expression mechanism of human bone marrow stromal cells (Ma *et al.*, 2015; Zhu *et al.*, 2017). Zn has antibacterial efficacy on both gram-positive *S. aureus* and gram-negative *E. coli* organisms. They damage the bacterial cell membrane by binding with the bacterial DNA (Bakhsheshi-Rad *et al.*, 2017). Su *et al.* (2019) stated that there is a change in the cell viability and biocompatibility among the various zinc groups like ZnP, ZnO and Zn hydroxide. The cell adhesion on the surfaces of the groups showed well-formed cell fattened spindle cellular morphology for ZnP group whereas the other groups showed round apoptotic cell morphology. The in vitro cell viability of the pre-osteoblasts seeded directly on the samples showed increased cell viability for ZnP group compared to other groups. Interfacial Zinc Phosphate is the key to controlling biocompatibility of metallic zinc implants. Jin *et al.* (2018) combined zinc with magnesium and formed an alloying element for arterial biodegradation. The magnesium was added at concentration of 0.002%, 0.005% and 0.008%wt with the zinc. The in vivo biocompatibility of the alloy was done on SD rats for a period of 1–11 months. The results showed that the increase in concentration of magnesium showed trends of decreased biocompatibility. The histological studies showed increased macrophages and giant cells owing to increased inflammatory reactions near the implant site for 0.008% Mg (Jin *et al.*, 2018).

Wang *et al.* compared the osteosynthesis efficacy of novel zinc alloy with PLLA and titanium for canine mandibular fracture model. The micro CT images after 4 weeks implantation showed more external callus formation for the PLLA group compared to the zinc and titanium. After 12 and 24 weeks of implantation the calluses in all group decreased and calcification and remodeling of new bone was seen. The zinc alloy had more bone volume, total bone density and trabecular thickness compared to the titanium and PLLA (Wang *et al.*, 2019) (Fig. 2(a and b)).

Ren *et al.* (2019) evaluated the corrosion and biocompatibility of Zn-xMg-0.5Zr alloy for orthopedic application. In comparison to pure Zn, addition of Mg and Zr showed good grain refinement, improved tensile strength and corrosion resistance. With an increase in the magnesium concentration from 1.5 wt% the corrosion of the alloy increased and the cytocompatibility decreased. With the addition of 0.5% and 1% magnesium, the corrosion rate was less and the cytocompatibility also increased. Histological analysis after 90 days post-implantation of Zn-1Mg-0.5Zr compared with SUS304 on the subcutaneous muscle of SD rats showed healthy perimysium and muscle fibers. There was no signs of inflammatory reaction or necrotic tissues surrounding the implants for both the groups. The histological results showed that Zn with the addition of Mg and Zr in less concentration showed good biosafety and are suitable for biomedical applications (Ren *et al.*, 2019). The long-term implantation of zinc alloys combined with aluminum for 20 months in abdominal rat aorta showed increased activity of macrophage penetration. The macrophages were able to penetrate the thick corrosion layer that was formed around the implants. The pure zinc group showed delayed macrophage entry into the corrosion layer. This is due to low corrosion rate with greater fibrous encapsulation around the implant. The addition of aluminum to the zinc increased the macrophage activity due to the intergranular corrosion (Guillory *et al.*, 2019, 2016).

Iron Alloy

Among the metals used for biomedical application, iron has the lowest tendency to dissolve. The daily dose of iron is 10 mg. The corrosion of Fe is mediated by dissolved oxygen. There is a protective surface oxide layer formed with iron when exposed to physiological fluid and this attributes to the lower corrosion rate and prevents rapid degradation (Bowen *et al.*, 2016) (Fig. 4). There is no negative inflammatory response or cell toxicity or thromboses when Fe biodegradable stents were tested on pigs and rats (Bowen *et al.*, 2016) (Table 7). The Fe stents can be easily deployed into the arteries due to its high radial strength which allows it to be made into extremely thin structures. Although Fe has good corrosion resistance property, the production of iron oxide by-

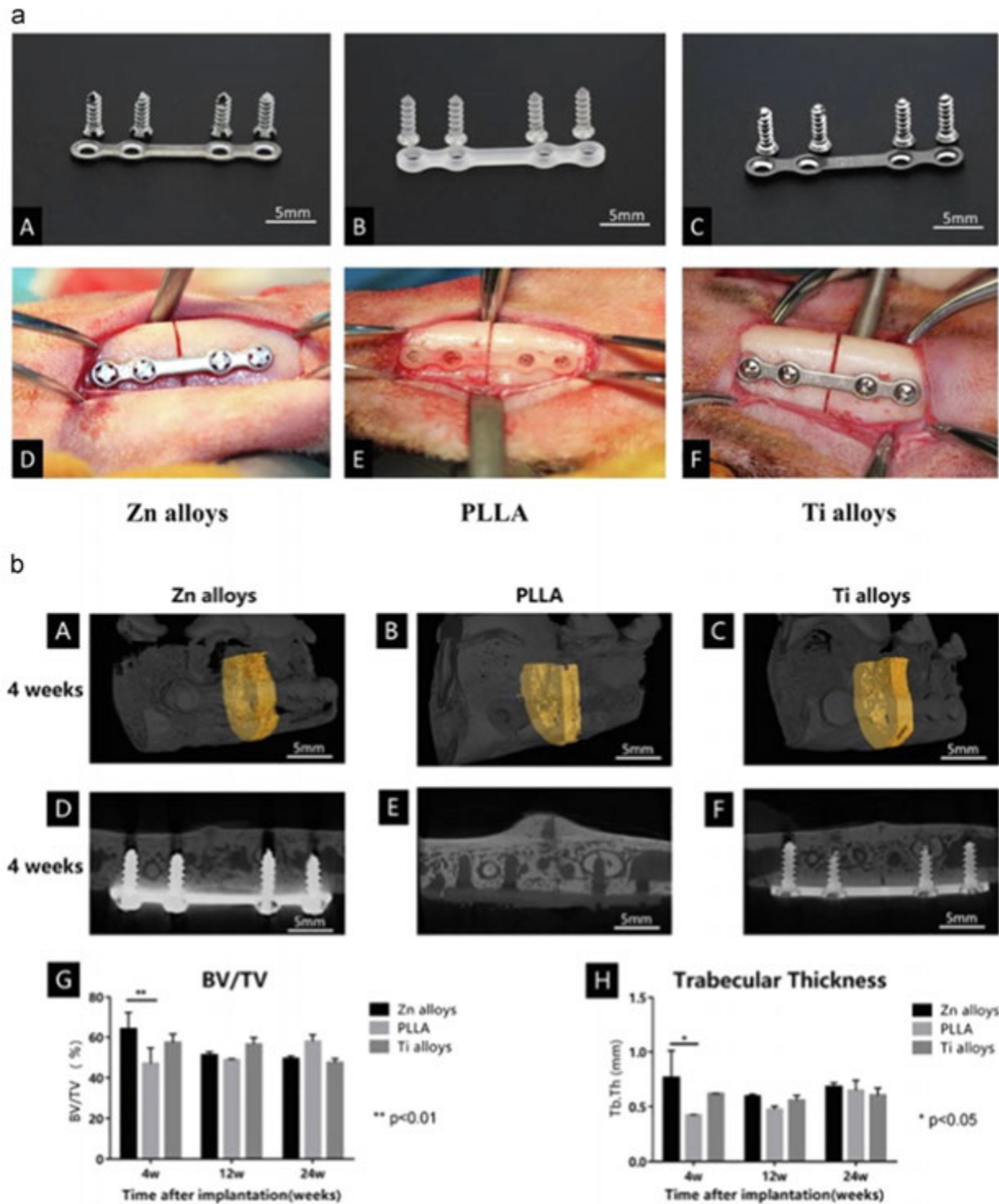


Fig. 2 **a:** (A) Zinc alloy plate and screws, (B) PLLA plate and screws, (C) titanium alloy plate and screws. All implants are in the same dimensions. (D, E, F) Fixed mandibular bone fractures immediately after surgery for the three groups. **b:** Micro-CT three-dimensional reconstruction images (A zinc alloy, B polylactic acid, C titanium alloy) 4 weeks after the operation. The yellow highlighted area is the selected region of interest (3 mm wide and 7 mm high). In the micro-CT cross-sectional images 4 weeks post operation, PLLA I formed significantly more external calluses than the zinc alloys (D) and titanium alloys (F). (G, H) BV/TV and Tb. Th comparison of the three groups; the zinc alloy group is significantly higher than the PLLA group at 4 weeks post operation. Reproduced from (a and b) Wang, X., *et al.*, 2019. In vivo study of the efficacy, biosafety, and degradation of a zinc alloy osteosynthesis system. *Acta Biomaterialia*. 92, 351–361.

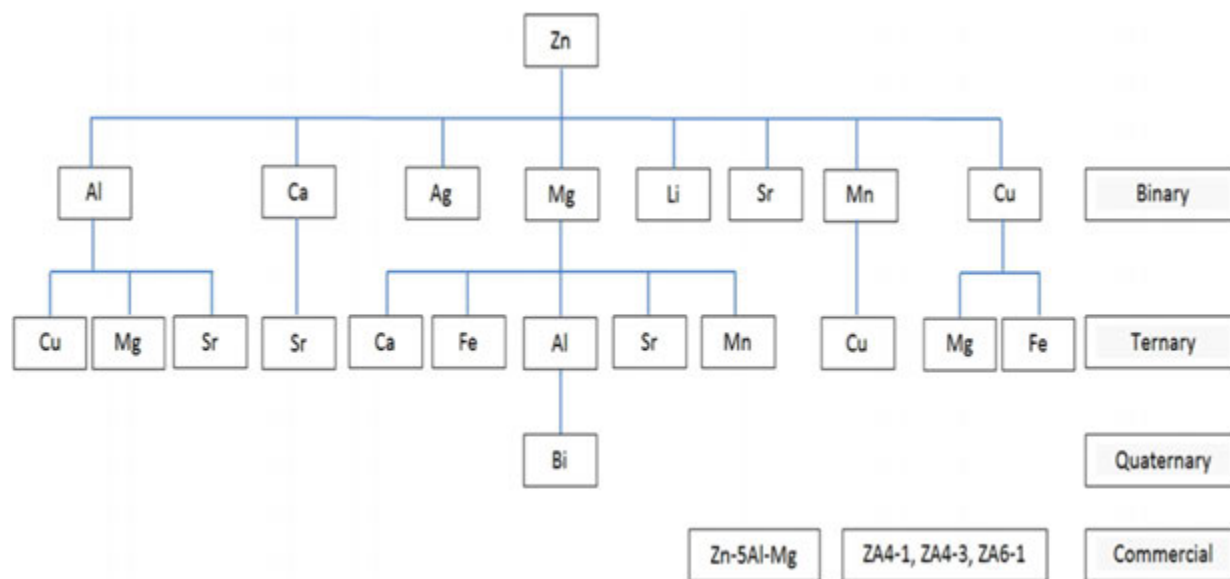


Fig. 3 Schematic showing the different Zn alloy combinations studied for biodegradable implant applications. Reproduced from Venezuela, J., Dargusch, M., 2019. The influence of alloying and fabrication techniques on the mechanical properties, biodegradability and biocompatibility of zinc: A comprehensive review. *Acta Biomaterialia* 87, 1–40.

products and influx of metallic ions into the surrounding tissues leads to cellular damage and cytotoxicity. The long-term overdose of iron [normal; 6–20 mg] may lead to cell damage by affecting the DNA, protein and lipid membrane. There is an increase in inflammation and free radicals leading to damage of lipid (Bowen *et al.*, 2016; Hong *et al.*, 2016). Iron implants may interfere with the MRI by heating up the implant due to the strong magnetic field. This leads to the change in the morphology of the implant and leaching of the iron particles. The displaced Fe particles exerts forces on the attached cells causing cell dragging and cytoskeletal changes and changing the intercellular signaling pathway. Further, iron used for load-bearing implant application may lead to stress shielding effect due to the differences in its properties and that of the natural bone. The slow degradation rate of iron reduces the tissue regeneration and prevents the forces transferring to the surrounding bone leading to stress shielding effect and failure of osteointegration (Ortolani *et al.*, 2016).

Liu *et al.* (2019) compared pure iron with iron bulk metallic glasses [Fe77m05P9C7.5B1.5] and investigated the antibacterial efficacy against *S. aureus* and *E. coli* and cytocompatibility of the composites with human umbilical vein endothelial cells [HUVE]. The composite inhibited bacterial growth mainly in *S. aureus* and without any changes in the *E. coli* and there were no signs of cytotoxicity to the HUVE cells (Liu *et al.*, 2019). Kraus *et al.* (2014) evaluated the degradation and toxicity of iron-based alloys [pure iron and Fe-10Mn-1Pd, Fe-21Mn-0.7C-1Pd] by implanting in the femur of SD rats over a time period of 52 weeks. The degradation process was very slow in all the groups with no significant difference between the groups. The oxygen transport around the implant was restricted by the dense layer of degradation products [Fe-oxides] around the implant surface. Although oxygen is necessary for the degradation of the iron, its availability away from the implant area is restricted by the degradation products surrounding the implants. There were no signs of local toxicity or clinically any abnormal changes in the tissues surrounding the implant site was noticed. The slow degradation rate of iron is still questionable to be used in temporary bulk implants (Kraus *et al.*, 2014). The cytocompatibility of Fe alloy [Fe-Mn-Cu] using MG63 cells showed increased cell viability at 72 h cell culture and showed flattened spindle elongated morphology without any signs of apoptosis (Mandal *et al.*, 2019).

Magnesium Alloys

Biodegradable metals are defined as any metals when placed within the body, has the ability to degrade completely with positive host response from the corrosion products thereby enhancing the tissue health without any material residue (Zheng *et al.*, 2014; Witte, 2010). Any metal can be considered biodegradable when it has a good corrosion rate within the body and the corrosion products released should be completely metabolized by the host body (Zheng *et al.*, 2014). There is a paradigm shift towards the use of biodegradable metals most importantly magnesium for their superior properties of preventing stress shielding effect. The use of magnesium dates back to 1878 when they were used for closure of blood vessels (Witte, 2010). Unlike the stainless steel commonly used for fracture plating, magnesium didn't show any signs of skin sensitization and had high tensile strength and elastic modulus nearly matching that of the natural bone (Witte and Eliezer, 2012). Magnesium is the fourth most abundant cation in the human body and acts as a cofactor for many enzymes (Witte and Eliezer, 2012). Magnesium is a light weight material with a density of 1.74 g/cm³. Although magnesium is considered to have higher superior properties, the corrosion rate of pure magnesium is high and needs addition of alloying element to control the corrosion rate. There are many factors which leads to the

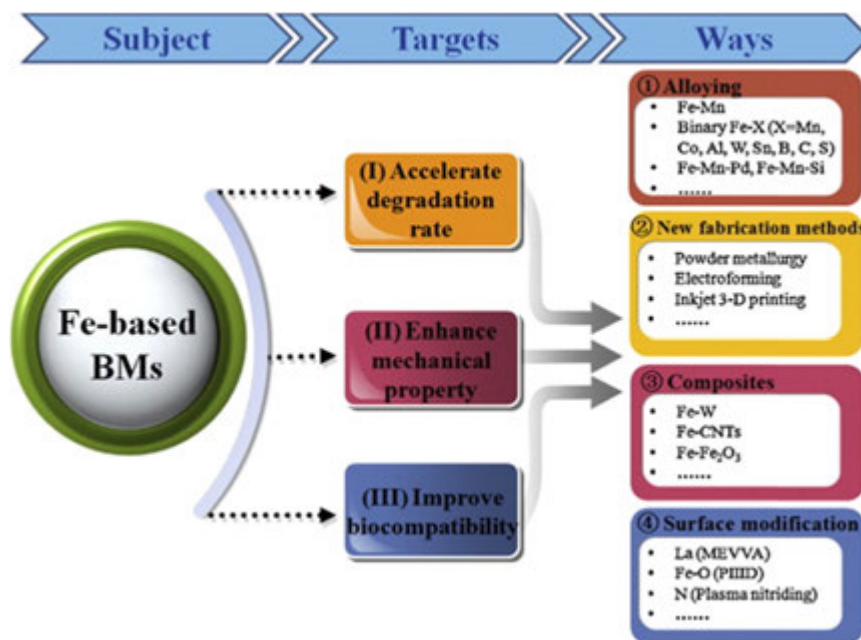


Fig. 4 Properties and composites of iron based biomaterials. Reproduced from Bowen, P.K., *et al.*, 2016. Biodegradable metals for cardiovascular stents: From clinical concerns to recent Zn-alloys. *Advanced Healthcare Materials* 5 (10), 1121–1140. Zheng, Y., Gu, X., Witte, F., 2014. Biodegradable metals. *Materials Science and Engineering: R: Reports* 77, 1–34.

increased corrosion rate of any metal placed as an implant within the body. One main factor among them is the pH of the body fluids. In cases of trauma and infection, immediately after the placement of implant within the body tissues, the pH of the surrounding area drops to 5.3–5.6 (Ebenezer *et al.*, 2015). The drop in pH activates the infectious microorganisms surrounding the implant area and reduces the oxygen concentration around the implant causing cellular damage. The depleted oxygen environment and pH increases the corrosion of magnesium leading to more degradation of the metal. The most possible way to reduce the corrosion of pure magnesium is by the addition of suitable alloying elements, processing methods and coatings which reduces the initial implant corrosion thereby sustaining the initial drop in the pH and oxygen levels surrounding the implant area. The addition of suitable alloying element to magnesium reduces the corrosion rate and allows a balance in time needed to new tissue/bone regeneration (Table 8). In compared to the in vitro, in-vivo corrosion observed is lesser due to the adherence of proteins and inorganic deposits like calcium phosphates which leads to further reduction in the corrosion rate (Prasadh *et al.*, 2019a; Witte and Eliezer, 2012). The corrosion of magnesium ions from the implant is quickly removed by the blood serum and the kidneys. The extracellular fluids contain a constant magnesium concentration of 0.7–1.05 mM. With the presence of high serum levels of magnesium ion concentrations of up to 6–7 mM, it leads to paralysis of the muscles, respiratory distress and cardiac arrest (Witte and Eliezer, 2012). The corrosion products released from the degraded magnesium are digested by the macrophages and the giant cells. The engulfed macrophages and the giant cells release inflammatory cytokines like IL-1 and IL-6 which further initiates the osteoclasts to begin the process of osteolysis (Lu *et al.*, 2002). Magnesium degrades releasing hydrogen gases which forms gas pockets when implanted in subcutaneous tissues, whereas no reports of gas pockets in intravascular stents were reported. This could be due to the fact that the diffusion and solubility coefficient of hydrogen gas released from the magnesium depends on the proteins, lipid content and glycosaminoglycans. The diffusion of hydrogen gas differs in stagnant and flowing fluids. That's the attributing factor of increased corrosion rates in an in vitro scenario compared to in vivo. In the further sections of this article we will be focusing on the various alloying elements added to the magnesium and how the elements affect the biocompatibility of the composites (Witte and Eliezer, 2012) (Table 9).

Classification of Mg alloying elements

Alloying elements of Mg can be categorized into five categories based on their characteristic features that affect the microstructure, mechanical properties, corrosion resistance, and biocompatibility of the Mg.

Bio-functional elements (Sr and Ca)

Sr has been reported as an osteoinductive element. It plays a key role by triggering the formation of new osteoblasts, thereby promoting rapid integration of the graft. Additionally, it is a biocompatible element that enhances the mechanical properties and the corrosion resistance of Mg alloys when the addition of Sr is $\leq 5\%$ (Li *et al.*, 2012).

Ca being the most abundant element in the human body is present in the form of the mineral HA in the skeleton. Studies have proved that any disturbance of Ca cation in the human body may possibly lead to severe pathological conditions. The additive

Table 7 Summary of animal tests for Fe-based biodegradable metals

Material	Animal model	Duration	Findings	References
Pure iron stent	Rabbits, descending aorta	6–18 months	No thrombogenicity, no significant neointimal proliferation and systemic toxicity, faster degradation at junctions of the stent; locally discoloration of intima	Peuster <i>et al.</i> (2001)
Pure iron stent	Porcine, descending aorta	360 days	Complete coverage of neointima after 14 d; accumulation of degradation product adjacent to the stent struts and within adventitia accompanied by macrophages; disintegration of struts after 1 year with large portions of the stent residue; no sign of iron overload or iron-related toxicity	Peuster <i>et al.</i> (2006)
Pure iron stent	Porcine, coronary arteries	360 days	Locally discoloration of the vascular wall adjacent to the stent; degradation was evidenced at 28 d; similar vessel parameters to Co–Cr stent	Waksman <i>et al.</i> (2008)
Pure iron stent	Rat, artery lumen or artery matrix	1–9 months	Fe wire experienced substantial corrosion within artery matrix, whereas experienced minimal bio corrosion in blood-contacting environment	Pierson <i>et al.</i> (2012)
Nitrided iron stent	Porcine, iliac arteries	12 months	A nearly intact endothelial cells layer formed on the stented vessel wall; a decreased inflammation scoring, ~30% loss of in-stent luminal diameter, ~47% reduced strut thickness and corrosion product accumulation 12 months post implantation	Feng <i>et al.</i> (2013)

Note: Bowen, P.K., *et al.*, 2016. Biodegradable metals for cardiovascular stents: From clinical concerns to recent Zn-alloys. *Advanced Healthcare Materials* 5 (10), 1121–1140.

amounts of Ca to Mg alloys should be limited to less than 1% because higher Ca content in Mg alloys will lead to the formation of a large volume of the secondary phase of Mg_2Ca , which diminishes the corrosion resistance of Mg alloys (Li *et al.*, 2010, 2008).

Biocompatible element (Zr)

Zr is established as an effective alloying element that improves the corrosion resistance and grain refinement of Mg alloys. This is essential in order to decrease the degradation rate of Mg alloys in vivo. Recent studies have indicated that the addition of Zr to Mg alloys should be limited to less than 5% (Li *et al.*, 2012).

Essential trace elements (Mn and Zn)

Mn and Zn are essential trace elements for the human body and they are usually used in Mg–Al alloys such as in AZ series. When it comes to using Mn and Zn as Mg alloying elements, concentration control has often been a significant consideration. Unfortunately, literature lacks any systematic research to define the concentration limits of Mn and Zn in biodegradable Mg alloys. Further studies are needed to elucidate the optimal concentrations of Mn and Zn in Mg alloys for a favorable combination of corrosion resistance, mechanical properties, biocompatibility and biodegradability that can be acceptable for load-bearing implant applications.

Toxic elements which should be avoided (Al, Li, Ce, Er, La, and Nd)

The accumulation of Al in the human body may be responsible for causing a disease process (Izumi *et al.*, 2009; Cases, 2005; Hirano *et al.*, 1993). Li is toxic to humans. A dose of 10 mg/L Li in the serum of humans could induce bipolar disorder, and with 20 mg/L Li in the serum there is a risk of death (Ferrante *et al.*, 2013). La (Feyerabend *et al.*, 2010; Tsuda *et al.*, 1992) and Ce (Bruce *et al.*, 1963; Scalbert *et al.*, 2002) showed a lower value of LD_{50} . Understanding the toxicological effects of Ce on the human body, it is seen that Ce tends to accumulate primarily in the bone, liver, heart and lung (Chen *et al.*, 2005). Nd being a light REE exhibits similar toxicity to La and Ce. Although Er belongs to the group of REEs with large ionic radii, it is moderately to highly toxic, causing writhing, ataxia, labored respiration, walking on the toes with arched back, and sedation (Ding *et al.*, 2014).

Results on the biocompatibility of Gd and Y are still inconclusive

Current studies demonstrates that Gd (Feyerabend *et al.*, 2010) and Y (Pogosova *et al.*, 2013) are potential alloying elements in Mg alloys for biomedical applications. Nevertheless, the toxicity of Gd appeared to be apparent as even 1% Gd chloride caused perinuclear vacuolization of the parenchymal cells of the liver, besides affecting bone quality and health (Darrach *et al.*, 2009). Y showed obvious toxicity due to the increased blood eosinocyte levels thereby causing eosinophil infiltration in the submucosa (Bruce *et al.*, 1963). Further research in the future can possibly reveal the effects of Gd and Y, outlining their concentrations on the microstructure, mechanical properties, corrosion resistance and biocompatibility of Mg alloys.

Table 8 Mechanical and corrosion properties of magnesium matrix composites

Material	Condition	UCS (MPa)	UTS (MPa)	YS (MPa)	Hard-ness (HV)	Elongation	I_{corr} (A/cm ²)	References
Mg – 2Zn – 0.5Ca/1 β -TCP	Normal Casting Mg – 2Zn – 0.5-Ca then remelted to add TCP						789.9 $\pm$ 8.8 CR* (0–36 h) mg cm ⁻² h ⁻¹	Huang <i>et al.</i> (2015)
β -Ca ₃ (PO ₄) ₂ /Mg-Zn	PM + extrusion			183			7 (μ A cm ⁻²)	Yan <i>et al.</i> (2017)
Mg-Bredigite 40 vol%	PM + extrusion	190			73			Dezfuli <i>et al.</i> (2017)
(a) Mg60 (b) Mg67 (c) Mg60T40 (d) Mg67T40	As-cast	580 440 800 700					~	Wong <i>et al.</i> (2017)
(a) Pure Mg (b) Mg0.5SiO ₂ (c) Mg1SiO ₂ (d) Mg2 SiO ₂		174 $\pm$ 7 220 $\pm$ 2 03 $\pm$ 10 207 $\pm$ 3			46 $\pm$ 3 53 $\pm$ 1 62 $\pm$ 4 69 $\pm$ 2			Parande <i>et al.</i> (2016)
Pure Mg Mg/0.58 TiO ₂ Mg/0.97 TiO ₂ Mg/1.98 TiO ₂ Mg/2.5 TiO ₂	As-cast	332 $\pm$ 10 285 $\pm$ 13 278.4 $\pm$ 8 297 $\pm$ 1 305.5 $\pm$ 1	156 $\pm$ 6 128 $\pm$ 3 154 $\pm$ 7 165.5 $\pm$ 3 170 $\pm$ 6		52 $\pm$ 1.5 58 $\pm$ 2 61 $\pm$ 2 64 $\pm$ 3 68 $\pm$ 1.5			Meena-shisundaram <i>et al.</i> (2015)
BG – 5/Mg BG – 10/Mg BG – 15/Mg	PM				42.5 47.5 49			Wan <i>et al.</i> (2016)
Mg-Mn-Zn-Zr Mg-Mn-Zn-Zr – 5HA Mg-Mn-Zn-Zr – 5BG Mg-Mn-Zn-Zr – 5HA Microcrystalline Mg	PM						1.62 $\times$ 10 ⁻⁴ 3.39 $\times$ 10 ⁻⁴ 1.49 $\times$ 10 ⁻⁴ 2.43 $\times$ 10 ⁻⁴ 3.34 $\times$ 10 ⁻⁴	Kowalski <i>et al.</i> (2016) Liu <i>et al.</i> (2017)
Mg-CS 10 wt% Mg-CS 20 wt% Mg-CS 30 wt% Mg-CS 40 wt% Mg-CS 50 wt%		178 235 232 212 170						Huan <i>et al.</i> (2016)
Pure Mg Pure Mg Mg – 5Hap Mg – 10Hap Mg – 15Hap	As-cast PM + extrusion PM + extrusion PM + extrusion PM + extrusion	20–115 340 222 219 216	108.3 $\pm$ 3.1			27.8 $\pm$ 0.8 9.6	Pure Mg	Del Campo <i>et al.</i> (2014)
Mg – 0.58(vol%) TiO ₂ Mg – 0.97(vol%) TiO ₂ Mg – 1.98(vol%) TiO ₂ Mg – 2.5(vol%) TiO ₂		285 278.4 297 305.5	128 154 165 170		58 61 64 68	10 10.8 11.5 10		Khalajabadi <i>et al.</i> (2015)

Table 8 Continued

Material	Condition	UCS (MPa)	UTS (MPa)	YS (MPa)	Hard-ness (HV)	Elongation	I_{corr} (A/cm ²)	References
Mg-HA-TiO ₂ -MgO		253				9.8	255	
AZ91-10FA	PM			86		5.78	7.4×10^{-5}	Razavi <i>et al.</i> (2010)
AZ91-20FA	PM			93		5.32	2.3×10^{-6}	
AZ91-30FA	PM			105		4.51	3.5×10^{-7}	

Abbreviation: MPa, MegaPascal, PM, Powder Metallurgy.

Note: Radha, R., Sreekanth, D., 2017. Insight of magnesium alloys and composites for orthopedic implant applications – A review. Journal of Magnesium and Alloys 5 (3), 286–312.

Table 9 Effects of alloy elements in biocompatible Mg alloys

Alloy elements	Mechanical properties	Path physiology	Toxicology
Ag	Increase tensile strength, corrosion resistance, antibacterial effect	Blood serum 11–26 g/L	Uncertain
Ca	Increase corrosion resistance and grain refinement	Presented in bones and teeth,	Metabolic disorder
Mn	Corrosion resistance improved	Blood serum level < 0.8 g/L, effects cellular functions, immune system, bone growth	Neurological disorder
Sr	Enhance bone mass and reduce the rate of fractures. Improves corrosion resistance and grain refinement	Presented 140 mg in human body 99% presented in the bones	Neurological disorder
Sn	Increase compressive strength and corrosion resistance	Located in higher levels 9–140 g/L in liver	Carcinogenic
Zn	Enhance yield stress; reduce	Required blood serum 12.4–17.4 mol/L level, necessary to enzyme and immune system	Neuro venomous and obstruct in bone development

Note: Radha, R., Sreekanth, D., 2017. Insight of magnesium alloys and composites for orthopedic implant applications – A review. Journal of Magnesium and Alloys 5 (3), 286–312.

This classification provides suggestions for the early stage of implant development and the selection of alloying elements. Interestingly, some of the alleged “toxic elements” used in alloying, such as Li, La, Ce and Nd, have been successfully applied in commercial Mg alloys for biomedical applications (Waksman *et al.*, 2006). Despite the perceived toxicity of these elements, they are still employed judiciously for various biomedical applications. There is no evident harmful or beneficial substance, and even pure water can kill at a sufficiently high dose (Yuen and Ip, 2010). Thus, the dose of alloying elements determines the associated toxicity levels. For instance, despite Sr being classified as a bio-functional element, excessive addition of Sr in Mg alloys deteriorates the corrosion resistance, and impairs the biocompatibility.

Concern of biocompatibility in alloying of Mg

An orthopedic Mg implant is characterized as any matter, structure, or surface that interacts with biological tissues, and is required to possess biomechanical compatibility with natural bone, an appropriate corrosion rate (i.e., degradation rate) to maintain mechanical integrity during healing and excellent biocompatibility making it harmless to host tissues. Following implantation, the Mg alloy implant would directly come in contact with the organics or tissues. In an in-vivo scenario, the reaction between metals and a physiological environment such as proteins, cations and anions triggers the degradation of Mg alloys. The biocompatibility of Mg alloys is determined by the alloying elements in most cases. Hence it is significant to select the Mg alloying elements that are essential for the human body. Approximately 96% of the human body is comprised of oxygen, carbon, hydrogen and nitrogen, which are present in the form of water and proteins (Chen *et al.*, 2012). The remainder 4% largely exists either in the bone and tooth as minerals (Ca, Mg and P) or in the body fluid and blood as electrolytes (Na, K and Cl), which are considered to be macro elements (VanPutte *et al.*, 2016). Besides the macro elements, lower concentrations of barium, beryllium, boron, cesium, chromium, cobalt, copper, iodine, iron, lithium, molybdenum, nickel, selenium, strontium, tungsten and zinc also exists. These elements are referred to as trace elements (Chen *et al.*, 2012). Researchers have revealed the potential of Ca, Li, Sr and Zn as alloying elements for biodegradable Mg alloys.

Recent researches have attempted to elucidate the biological performance of Mg alloys when combined with these elements or with other traditionally used alloying elements such as Al, Mn and Zr, and REEs to be employed for biodegradable Mg alloy implant materials. Certain significant pre-requisites of an ideal Mg implant material includes their ability to be non-toxic and not cause any inflammatory and immunogenic responses. The Mg alloys should have minimal deleterious effects and these should be short term as much as possible. Nevertheless, in the actual application process, this ideal situation is not always attained. However, it is often a mandate to ensure that the composition of Mg alloys does not impose a significant hazard to the human body.

Table 10 Summary of animal tests of Mg alloy implants within bone

<i>Implants</i>	<i>Implantation site</i>	<i>Period/ weeks</i>	<i>New bone</i>	<i>Bone contact</i>	<i>Gas cavity</i>	<i>Degradation rate/mm/yr or residual implant %</i>
AZ31/gravity cast, rod AZ91/gravity cast, rod WE43/gravity cast, rod LAE442/gravity cast, rod	Marrow cavity, guinea pig	18	+	+	+	0% 30 vol%
AZ91/cast, rod AZ91 + PCL/cast, rod	Femoral diaphysis, rabbit	8	+	+	–	67 vol% 95–100 vol%
AZ31/extruded, screw	Hip bone, sheep	12	+	+		Main body
Mg–Sr/rolled, rod	Marrow cavity, mice	4	+	–	+	1.01 mm/yr
LAE442/extruded, rod LAE442 + MgF ₂ /extruded, rod	Femoral condyle, rabbit	12	+	–	–	0.31 mm/yr 89 vol% 0.13 mm/yr
LAE442/extruded, rod				–	–	79 vol%
Mg–0.8Ca/extruded, rod, smooth Mg–0.8Ca + MgF ₂ /extruded, rod	Marrow cavity, rabbit	24	+	+	–	74.67 vol%
Mg–0.8Ca/extruded, rod, smooth, sand blast, threaded	Femoral epicondyle, rabbit	28	+	–	+	V_{corr} , sand blast > threaded > smooth
Mg–0.8Ca/extruded, screw	Transcortical implantation in tibia, rabbit Muscle Cortex Marrow cavity	8	+		+	91.23 vol% 98.63 vol% 91.18 vol%
Mg–Ca/cast, screw	Femoral diaphysis, rabbit	12	+	–	+	1.27 mm/yr 20mass%
Mg–6Zn/extruded, rod	Femoral diaphysis, rabbit	14	+	–	+	2.32 mm/yr 13%
Mg–Mn–Zn/extruded, rod	Femoral diaphysis, rat	18	+	–		46%
Mg–Mn–Zn + Ca–P coating/ extruded, rod	Femoral diaphysis, rabbit	4	+	+	–	Main body
Mg–2Zn–0.2Ca/extruded, rod Mg–2Zn–0.2Ca + MAO + DCPD/ extruded, rod						
Mg–5Zr/cast, rod Mg–1Zr–2Sr/cast, rod	Tibia, rabbit	12	+	–	+	V_{corr} , Mg–1Zr–2Sr > Mg–5Zr and Mg–2–5Sr
Mg–2Zr–5Sr/cast, rod Mg–Y–Nd–HfRE*/–, rod	Femoral diaphysis, rat	24	+	+	–	Main body
WZ21/extruded, pin			+	+		
ZX50/extruded, pin	Femoral diaphysis, rat	24	+	–	+	V_{corr} , WZ21 < BMG < ZX50
MgZnCa BMG/cast, pin			+	+		
Mg–5Bi–1Ca/RS, rod	Femoral condyle, rabbit	4	+	–	+	1.85 mm/yr
AZ91D scaffold/porosity 72%–76%	Condyle, rabbit	12	+	–	+	0%

Note: Zheng, Y., Gu, X., Witte, F., 2014. Biodegradable metals. Materials Science and Engineering: R: Reports 77, 1–34.

The effect of commonly used alloying elements

Alloying and surface treatments of magnesium used for biomedical applications is the most suitable method to corrosion rate until the tissue/bone is completely regenerated. The most commonly used nutrient elements used for alloying with magnesium are zinc (Zn), calcium (Ca), manganese (Mn) and strontium (Sr). Al possesses certain excellent effects on the refining of the microstructure and enhancement of corrosion resistance, which makes it the most widely used element for Mg alloys (such as AZ21, AZ91D and AZ31). However, medical research has revealed that accumulation of Al in the brain may harm the intelligence and cause neuropathological relevant issues (Krewski *et al.*, 2007), and can also account for the development of Alzheimer's disease (Carter, 2010). It is understood that with increasing age, Al tends to accumulate in the tissues, and the increasing concentration of Al eventually results in the aggregation of β -amyloid, a factor leading to the formation of pathologic lesions in Alzheimer's disease (Krewski *et al.*, 2007). Furthermore, Al has a significant impact on immunology, and studies have shown that the vaccines containing Al may lead to lymphocyte and inconspicuous muscle fiber damage (Cases, 2005). The total body burden of Al in healthy adults is 30–50 mg and the safe dose of Al containing medications can permit a much larger amount of Al than in

Table 11 Summary of animal tests and clinical trial of Mg alloy stent within blood vessels

Usage	Alloy	Biocompatibility	Degradation	References
Animal test	AE21 stent (pig, coronary artery)	40% loss of perfused lumen diameter between days 10 and 35 due to neointima formation; a 25% re-enlargement between days 35 and 56 caused by vascular remodeling	Linearly degradation ~ 89 d	Laing (1979)
	WE43 stent (minipig, coronary artery)	The struts are covered by neointima after 6 d; higher minimal lumen diameter on week 4 and 12 than the 316L stent group	~ 98 d	Ma <i>et al.</i> (2016)
	AMS (preterm baby, pulmonary artery)	Normal serum Mg level on 72 h, persisted left lung perfusion throughout the 4-month follow-up, clinical tolerable to baby	~ 5 months	Witte (2010)
Pediatric use	AMS (newborn baby, aortic arch)	Restenosis after 3 weeks implantation; implantation of a 2nd AMS; the stent struts were substituted by a jelly-like CaPO ₄ compound and fibrotic structure; flexible stent segment	–	McBride <i>et al.</i> (1989)
	AMS (2-month-old girl, aorto-pulmonary collateral)	Restenosis after 4 months implantation of AMS	–	Mayer (1931)
	AMS (20 patients, 23 stents, lower limb vascular)	A low immediate elastic recoil; 89.5% primary clinical patency after 3 months and 72.4% after 24 months; no blood or vessel toxicity	–	Song and Shayan (1998)
	AMS INSIGHT (60 patients, 74 stents, lower limb vascular)	Lower angiographic patency rate 31.8% for AMS treatment and comparable complication rate 5% with PTA treatment (patency 58%, complication rate 5.3%)	~ 4 months	Zhang <i>et al.</i> (2010)
Clinical trial	PROGRESS-AMS (63 patients, 71 stents, 8 centers, coronary artery)	Restenosis caused by stent recoil and intra- and extra-stent neointima at 4 months; the neointima decreased after over 12 months; No myocardial Infarction, subacute or late thrombosis, or death occurred	~ 4 months	Li <i>et al.</i> (2008), Xin <i>et al.</i> (2008)
	BIOSOLVE-I DREAMS (46 patients, two cohorts, cohort 1 for 6 months and 2 for 12 months)	7% rate of target lesion failure, 4.7% revascularization rate, no significant change of vasoreactivity between 6 and 12 months, reduced lumen loss from 6 month to 12 month, no death and no thrombosis	–	Haude <i>et al.</i> (2013)

Note: Zheng, Y., Gu, X., Witte, F., 2014. Biodegradable metals. Materials Science and Engineering: R: Reports 77, 1–34.

the diet, possibly as high as 12–71 mg kg^{−1} per day (Keith *et al.*, 2008). Literature demonstrates that the exceeding doses have various adverse effects in humans (Verstraeten *et al.*, 2008) (Tables 10 and 11).

Ca is the most abundant element in the human body, occurring in the form of Ca²⁺ and present as the mineral HA in the skeleton (Renkema *et al.*, 2008). Its addition to the Mg alloys is useful for biomedical applications. Results of one study showed that the degradation media of the Mg alloys over 6 days had no influence on cell viability whenever they employed an Mg–Ca alloy, owing to the excellent biocompatibility rendered by the less than 1.2% of Ca used in the alloy (Feser *et al.*, 2011). Jung *et al.* (2012) reported that needle-type calcium phosphates similar to HA formed at the interface of Ca-containing implants and biological tissue, providing a progressive biological environment for bone mineralization. Ca also plays a crucial role in bone disease and soft tissue calcification (Viriyavejikul *et al.*, 2007). Normally, Ca is present at a level of 0.919–0.993 mg/L in the normal blood serum (Johnson and Riechmann, 1968). The recommended Ca dietary allowance for adults is approximately 1000 mg per day (Ilich and Kerstetter, 2000). Any disturbance of Ca cation in the human body may lead to severe pathological conditions, such as hypercalcemia and hypocalcaemia (Lopez *et al.*, 2009). Furthermore, an excess of calcium and phosphate absorption results in vascular calcifications, an important contributing factor for cardiovascular disease associated with kidney disease (Toussaint and Kerr, 2007). Another concern of Mg–Ca alloys is the formation of an insoluble corrosion product on the surface. Kirkland *et al.* pointed out that the insoluble “chalk like” product could become problematic to the human body if large amounts are formed (Kirkland *et al.*, 2010).

Alloying of calcium along with magnesium forms a stable intermetallic phase and improve the strength, creep properties and modifies the microstructure thereby reducing the corrosion. The acceptable level of biocompatibility when calcium added to magnesium is <= 1 wt%. Makkar *et al.* (2018) studied the in vitro degradation and in vivo biocompatibility of Mg–X Ca (X= 0.5 or 5 wt%) in rabbit model. The addition of 0.5 Ca showed increased new bone formation and biocompatibility compared to Mg–5Ca alloy. The initial corrosion rate was high for Mg–5Ca alloy compared to Mg–0.5Ca alloy. This could be the attributing fact in the biocompatibility of both the alloys (Makkar *et al.*, 2018). Li *et al.* (2008) combined Ca with magnesium with Ca content from 1 to 20 wt%. The alloy of Ca content was brittle when increased from 5 to 20 wt%. The cytotoxicity evaluation using L929 fibroblast cells showed Mg–1Ca alloys didn’t not show any signs of toxicity and the cell viability was also increased. Whereas by increasing the Ca concentration from 5 to 20 wt% showed reduced cell viability and increased cytotoxicity (Li *et al.*, 2008). Mohamed *et al.* (2019) studied the in vitro degradation and cytotoxicity of 0.8 wt% Ca addition to Mg. The addition of 0.8 Ca to Mg showed a reduced corrosion rate compared to pure Mg and there was slight increase in the cell proliferation and cell viability compared to pure Mg when tested on HEK 293 human derived stem cells. This is attributed to the fact that the formation of

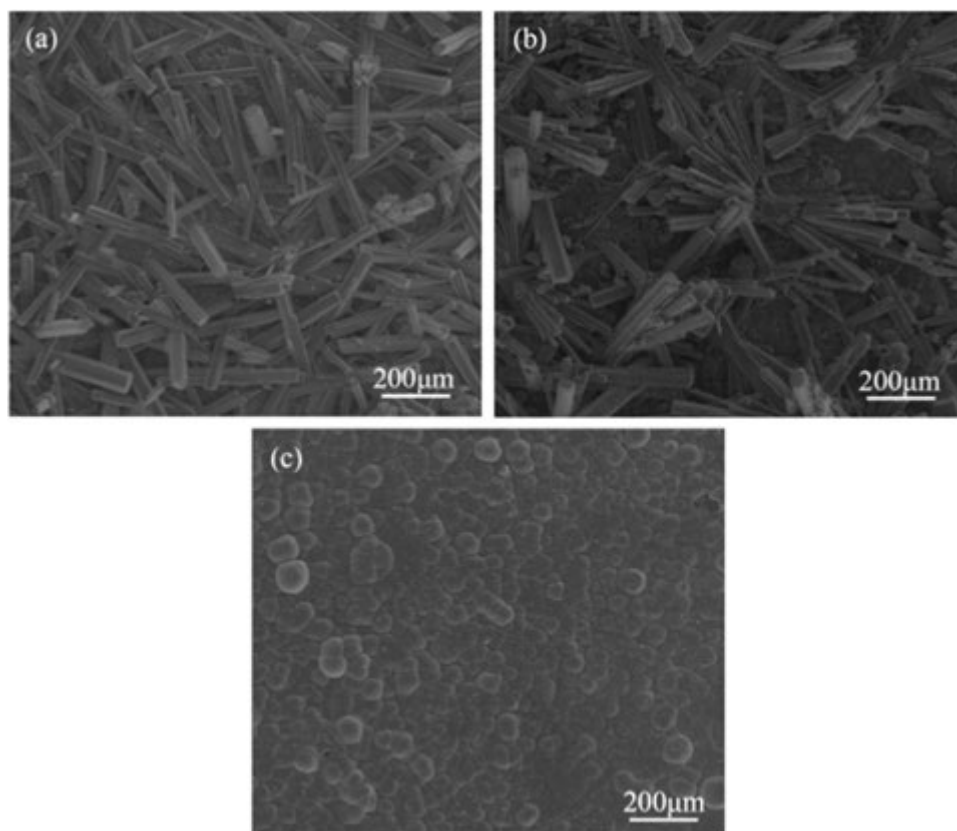


Fig. 5 SEM micrographs of (a) Mg/1Ca, (b) Mg/5Ca and (c) Mg/10Ca composite samples after 72 h immersion in DMEM. Reproduced from Zheng, Y., *et al.*, 2010. In vitro degradation and cytotoxicity of Mg/Ca composites produced by powder metallurgy. *Acta Biomaterialia* 6 (5), 1783–1791.

carbonated hydroxyapatite crystals on the implant surfaces mimics the bone apatite crystal and reduces corrosion rate (Mohamed *et al.*, 2019). Liu *et al.* (2015b) evaluated the biosafety and corrosion products of Mg-30% Ca alloys. Black powder precipitate particles and small amount of white precipitate particles were released when the Mg-30%Ca degraded. The black powder particles were made of outer shell of Mg (OH)₂, MgO and Mg/Ca mixture. The cell cytotoxicity studies done with L929 fibroblasts showed no signs of cytotoxicity and cell apoptosis. The morphology of the cells was flattened and spindle shape (Liu *et al.*, 2015b). Zheng *et al.* (2010) studied the cytotoxicity of Mg/Ca alloy produced by powder metallurgy against L929 fibroblast cells. The cell viability results on day 1 and day 4 showed no significant difference between the 1, 5 and 10 Ca concentrations whereas on day 4 the Mg-10 Ca showed 40% decrease in cell viability and change in the morphology of cells from flat spindle to round cells. Cell cytotoxicity could be due to the increase in corrosion rate of Mg-10 Ca alloys compared to 1 Ca and 5 Ca alloys (Zheng *et al.*, 2010) (Fig. 5).

The discovery of Li drew a lot of attention for its characteristic of being potential alloying element. Li inhibits the functioning of multiple enzymes in the body thereby striking numerous effects in humans and in other organisms (Yang and Xi, 2016). (Giles and Bannigan, 2006) reported that Li was a teratogenic hazard to the cardiovascular system of the human body, following his study on mice and rats where they observed their ability to produce skeletal and craniofacial defects following the administration of Li. Aral and Vecchio-Sadus (2008) investigated the toxicity of Li to humans and found that doses of Li (10 mg/L in serum) in humans induced bipolar disorder, and at 20 mg/L Li in the serum there is a risk of death. These studies further demonstrate the specific toxicity of Li presenting with several features such as acute abnormalities from Li poisoning and chronic changes such as nephrogenic diabetes insipidus, epithelial cell disease, and chronic kidney disease.

Mn is an essential trace element for physiological processes, and it is a necessary element for the immune system and a variety of enzymes (Erikson *et al.*, 2005). However, Mn toxicity, such as cytotoxicity and neurotoxicity, has also been reported (Ding *et al.*, 2014; Erikson *et al.*, 2005; Ding *et al.*, 2011). Ding *et al.* (2011) assessed the cytotoxicity of Mn on sensory hair cells, auditory nerve fibers and spiral ganglion neurons in three rats isolated from birth. The results showed that the sensory hair cells were vulnerable to Mn toxicity. Disservice was observed with Mn absorption as low as 10 µM. Preponderant clinical and basic research concerning the toxic actions of Mn has primarily focused on central nervous system effects (Ding *et al.*, 2011). Data from a recent report showed that the abnormal verbal and visual memory functions of a 10 year old boy were aggravated with excessive exposure to well water containing a modest level of Mn (Woolf *et al.*, 2002). Additionally, it was found that the neurotoxicity also presented on

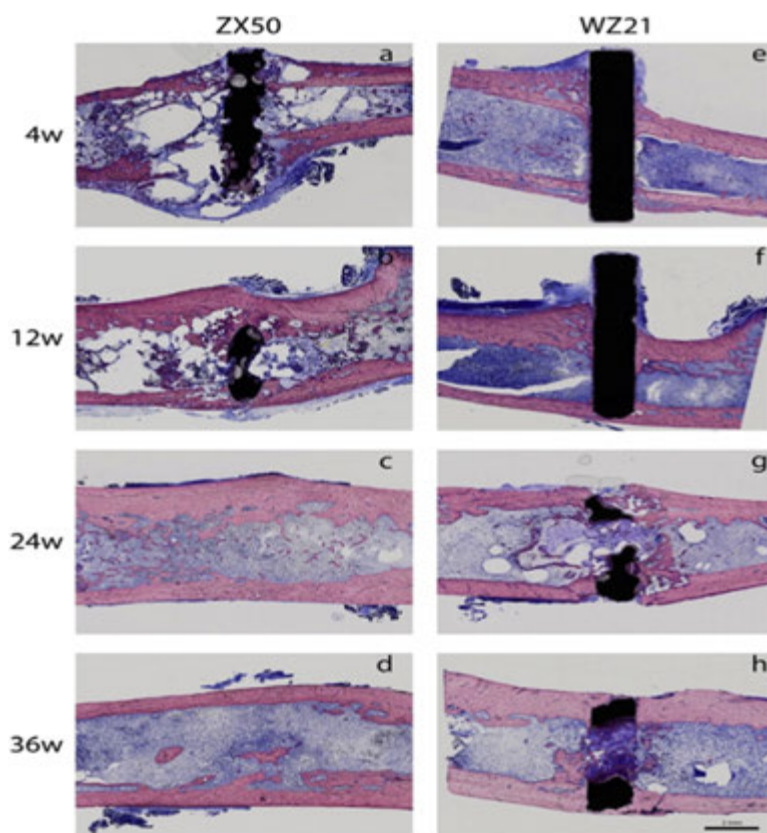


Fig. 6 Histological thin slides of ZX50 (a–d) and WZ21 (e–h) pins in a Lévai-Laczko staining. WZ21 represents the positive properties of Mg alloys by enhancing new bone formations around the implant. Even in the case of massive callus formation and release of high amounts of gas (a) the bone shows no permanent harming. Reproduced from Kraus, T., *et al.*, 2012. Magnesium alloys for temporary implants in osteosynthesis: In vivo studies of their degradation and interaction with bone. *Acta Biomaterialia* 8 (3), 1230–1238.

the induction factor of a disease with similar properties to those of Parkinson's disease (Bock *et al.*, 2008). Considering these findings for the toxicity of Mn, one has to take significant precautionary measures when using Mn as the alloying element in Mg alloys for biomedical applications.

Zn is also a trace element in the human body and a co-factor for optional enzymes in bone and cartilage (Brandão-Neto *et al.*, 1995). According to the U.S. Department of Health and Human Services, the recommended dietary allowance for Zn is 11 mg per day for men and 8 mg per day for women, where the corresponding burden of Zn is approximately 0.16 mg kg^{-1} per day for men and 0.13 mg kg^{-1} per day for women (Roney *et al.*, 2006). Various studies have revealed the negative consequences of an overdose of Zn intake on growth, development and health (Gürsel *et al.*, 2012; Kailerich *et al.*, 1980; Lastra *et al.*, 2001; Weigand and Boesch-Saadatmandi, 2012). It has been shown that the divalent metal can also lead to neurological disorders (Brandão-Neto *et al.*, 1995; Fosmire, 1990). Zn cation acts as a mediated inhibitor of neurotrophins, and can even lead to cell death (Isabel Post *et al.*, 2008). Hence an accumulation of Zn in the human body may induce embryonic motor neuron death and thereby affect mature motor neurons (Isabel Post *et al.*, 2008). Thus, a normal Zn concentration is essential to maintain body health. In contrast, when a large amount of Zn was implanted into the body in the form of an alloying element in Mg alloys, the toxicity could be seen as possibly impairing the immune function (Fosmire, 1990). Thus, it is highly essential to understand the possible complications of using these alloys with Zn, and taking measures to control the concentration of the alloying element to be added in the Mg alloys.

Chen *et al.* (2011) compared the in vitro and in vivo biocompatibility of Mg-Zn alloy with Polylactic acid [PLLA] for orthopedic applications. The cell results showed improved cell attachment, mineralization and osteogenic gene expression for Mg-Zn alloys compared to PLLA. The gene expression for collagen1 was more for Mg-Zn alloy. The in vivo implantation of the samples in the femoral bone marrow cavity of rabbits after 12 weeks implantation showed more new bone formation for Mg-alloy compared to PLLA (Chen *et al.*, 2011).

Kraus *et al.* (2012) compared the in vivo degradation and osteosynthesis of magnesium pins implanted in the femoral region of SD rats made of two different alloys, ZX50 and WZ21. The results were evaluated after implantation of 4 weeks to 24 weeks. The results showed that ZX50 pins showed faster degradation with large amount of hydrogen gas volumes at 4 week there were signs of inflammation around the implants and callus formation and new bone growth was slow. Whereas WZ21 pins showed gradual degradation and less hydrogen gas volumes and the formation of new bone was fast and there was no harm in bone regeneration. The WZ21 pins showed excellent biocompatibility with no signs of inflammation (Kraus *et al.*, 2012) (Fig. 6). Ding *et al.* (2019)

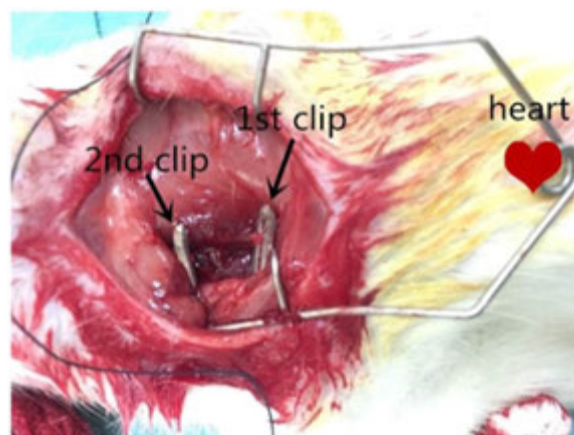


Fig. 7 Clip occluded carotid blood vessels of rats showing no blood leakage post-surgery. Reproduced from Ding, P., *et al.*, 2019. In vitro and in vivo biocompatibility of Mg–Zn–Ca alloy operative clip. *Bioactive Materials* 4, 236–244.

used Mg–3Zn–0.2Ca alloy for artificial clips for ligating the carotid artery in SD rats. There was no blood leakage after post-surgery and there were no signs of inflammation during clip degradations and histological analysis and blood biochemical parameters showed no signs of inflammation. The in vitro analysis on L929 showed no cell toxicity (Ding *et al.*, 2019) (Fig. 7).

Wong *et al.* (2019) compared the osteogenic capacity and biocompatibility of Mg–Zn–Ca bulk metallic glasses with titanium alloy and PLLA. There were 80% cell survival rates for all the groups in lower concentrations of the extract media. The Mg₆₀Zn₃₅Ca₅ BMGC showed excellent biocompatibility compared to the Ti and PLLA when implanted in the rabbit femur for 24 weeks. The magnesium alloy showed more new bone formation compared to the other groups and less inflammatory cells. There was very limited bone formation observed in the PLLA group (Wong *et al.*, 2019). The use of Zr in Mg alloys had been reported by few studies, as an effective alloying element to improve corrosion resistance and grain refinement (Gu *et al.*, 2011a; Huan *et al.*, 2010). A recent study on the biocompatibility of Mg–Zr–Sr alloys showed that Mg alloys with an addition of Zr up to 5% exhibited excellent biocompatibility and no adverse effect was observed after implantation into rabbits (Li *et al.*, 2012). The good biocompatibility of Zr in Mg alloys was supported by another study on the Mg–Zr–Ca alloys, which indicated that an Mg alloy with an addition of 1% Zr and 1% Ca exhibited promising compressive strength, good corrosion resistance and excellent biocompatibility (Li *et al.*, 2011; Zhou *et al.*, 2013). Yamamoto *et al.* (1998) investigated the cytotoxic evaluation of 43 metal salts including ZrCl₄ using murine fibroblasts and osteoblastic cells and found that Zr⁴⁺ had relatively low cytotoxicity, although it was reported that a high dose through oral administration (2250 mg kg^{−1} per day) of an aqueous solution of Zr oxychloride to mice induced chromosomal abnormalities in bone marrow cells (Yamamoto *et al.*, 1998). In another study by Delongea *et al.* (1983), it was shown that Zr oxychloride did not influence the growth curve after repeated administration of a dose of 230 mg kg^{−1} per day, and Zr oxide has been found to be non-toxic in animal studies using mice and rats. The aforementioned findings indicate that Zr is promising in alloying biodegradable Mg alloys, nevertheless the fact that the biocompatibility of Zr depends on the applied dosage and Zr ions formed in the usage mandates further scrutiny (Delongea *et al.*, 1983).

Currently, researchers are trying to pursue better biocompatible elements to replace traditional, less biocompatible alloying elements in Mg alloys such as Al, Zn, Mn, etc, so as to develop new implants with improved biocompatibility. It has been reported that Sr can reanimate bone cells and benefit postmenopausal osteoporosis as it can increase bone formation (Atkins *et al.*, 2009; Marie, 2005; Naveau, 2004; Nielsen, 2004). Sr is a plant growth stimulant, possessing similar functions to Ca. Leveraging these advantages, Sr has been introduced into Mg alloys for biomedical applications. The biocompatibilities of binary Mg–Sr alloys with various amounts of Sr content were studied in vitro and in vivo (Bornapour *et al.*, 2013). An Mg alloy with the addition of 2% Sr showed promoted bone mineralization without inducing any significant adverse effects. Novel Mg–Zr–Sr alloys with improved corrosion resistance, mechanical properties and biocompatibility have been successfully manufactured and investigated in vivo and in vitro (Li *et al.*, 2012). The findings have concluded that the addition of Sr in Mg alloys leads to an improvement of in vivo biocompatibility, especially for the promotion of bone formation. In his study, Bornapour *et al.* (2013), showed that a Sr-substituted HA layer, known to improve cell growth and tissue healing around bone implants, presented at the interface between the alloy matrix and the corrosion products, after implantation of the binary Mg–Sr alloys into a rabbit.

Rare Earth Elements (REEs)

Current literature showcases numerous desirable advantages of REEs in Mg alloys, namely improved corrosion resistance and electrochemical behavior, and enhanced mechanical properties (Al-Samman and Li, 2011; Bayani and Saebnoori, 2009; Birbilis *et al.*, 2011). In most cases, standard Mg–REE alloys contain more alloying elements than their designations (Al-Samman and Li,

2011). Almost any REE-containing Mg alloy contains more than one trace REE, such as LAE (containing Li, Al and REEs) and WE (containing Y and other REEs) (Bayani and Saebnoori, 2009). It is further understood that the in-vivo degradation directly links the alloying elements of Mg alloys to the released metal ions and the corrosion products. The effects of REEs on the biological behavior of Mg alloys are crucial in implant applications and should be investigated thoroughly.

Until today, REEs-containing Mg alloys are the most successful of the developed Mg alloys for biomedical applications. For instance, WE43 has been successfully used in biomedical application. Once an Mg alloy is implanted in vivo, the alloying elements come into direct contact with cells and eventually react with the tissues. The physical and chemical properties of the elements well as the ionic size of alloying elements determines whether an element is retained by the cells or whether the element triggers a reaction. Thus, cell culture in vitro seems to be an effective experimental approach to determine the impacts produced by the alloying element. The short-term effects on various cells by REEs such as Y, Nd, Dy, Pr, Gd, La, Ce and Eu were studied in detail by Feyerabend *et al.* (2010) suggested that La and Ce displayed the poorest biocompatibility with the highest cytotoxicity on cells, whereas the highly soluble Dy and Gd seem to be more suitable. According to Nakamura *et al.* (1997) REEs can be chemically classified into three groups on the basis of their ionic radii: (1) light REEs: La, Ce and Pr, (2) medium REEs: Nd, Pm, Sm, Eu and Gd, and (3) heavy REEs: Tb, Dy, Ho, Er, Tm and Yb. The light REEs, Ce and Pr, usually induce severe hepatotoxicity, including symptoms of fatty liver and jaundice; medium REEs are mainly distributed into the spleen and lungs (Nakamura *et al.*, 1997). Longerich *et al.* (1991) investigated the effect of Y and Ce on the behavior of humans. His findings indicated that concentrations of Y and Ce in the drinking water of mothers with neural tube defect infants were higher than in the mothers of normal infants, indicating that the absorption of REEs is not only dependent on the concentration but also the size of the elements. Basar *et al.* (2010) investigated the biocompatibility of HA doped with Y^{3+} (2.5, 5 and 7.5 mol%) and F^{-} (2.5 mol%) ions based on the cellular response of the control group with pure HA and found that HA doped with 2.5 mol% Y^{3+} had the highest cell density compared with other Y-containing HA. The cell proliferation on 2.5 Y-HA was close to that of the control group. Loos *et al.* (2007) investigated the biocompatibilities of an absorbable Mg stent with Y and some REE additives in vivo and in vitro. He demonstrated that Mg alloys without Al but containing small amounts of Y and REEs would be appropriate for biomedical applications. All the above studies indicate that Y is a particularly disputed alloying element, and it is essential to further investigate the effect of the addition of Y in Mg alloys on biocompatibility. Besides cell culture studies, literature presents other studies that tested the toxicity of REEs. These studies that were performed on small animals chiefly involved the administration of REE-containing salts such as chloride REEs or nitrate REEs via intravenous injection, inhalation and orally (Kawagoe *et al.*, 2005). Tsuda *et al.* (1992, 1995) conducted a series of studies on the short-term effects of elements La, Y and Eu on rats fed with hydrated chloride. By comparing the responses of these three REEs with different oral doses of 0, 40, 200 and 1000 mg kg^{-1} for 28 successive days, results indicated that the biological effects of Y were very similar to those of La except for the accumulating patterns and volumes, while Eu showed an obvious irritation effect as hyperkeratosis of the forestomach and eosinocyte infiltration of stomach submucosa were found in both males and females receiving a dose of 1000 mg kg^{-1} $EuCl_3 \cdot 6H_2O$ (Tsuda *et al.*, 1992, 1995).

Magnesium Metal Matrix Composites

Magnesium based composites are currently being investigated for possible use in human body as temporary implants. Literature search has shown that magnesium based composites exhibit improved mechanical strength, superior grain refinement and reduced corrosion rates (Tables 8 and 12). Most of the reinforcement added to magnesium alloys have proven to be biocompatible and used for biomedical applications. The bioactive and bioinert reinforcements like Al_2O_3 , ZrO_2 , HAp, SiO_2 , β -TCP and bio glass have been utilized. To note that ceramics used for bio-applications are termed as bio-ceramics. The bio-ceramics are traditionally categorized into three groups: bioactive, biodegradable and biocompatible ceramics.

The calcium phosphate particles (CPP) which resembles the natural bone composites are added to the magnesium for use in biomedical and orthopedic applications. The calcium phosphate particle are osteoconductive and reacts with the physiological body fluids and helps in new bone formation (Song *et al.*, 2009; Wang *et al.*, 2008). The calcium phosphate particles reduce the degradation rate in physiological fluids and release the degradation products like Ca^{2+} , HPO_4^{2-} and PO_4^{3-} (Zheng *et al.*, 2010). The reinforcement of calcium phosphate to magnesium alloy showed decreased degradation rate and increased mechanical strength (Goh *et al.*, 2005; Habibnejad-Korayem *et al.*, 2009; Zhong *et al.*, 2007).

Magnesium - HAp composites have been used for various biomedical applications. Gu *et al.* reinforced Mg with various amounts of HAp (10 wt%, 20 wt%, 30 wt%) and studied the corrosion and cytotoxicity of the composites (Gu *et al.*, 2011b, 2010). The addition of 10 wt% HAp increased the tensile strength and showed less corrosion rates when compared to composites with higher amounts of HAp (20 and 30 wt%). The cytotoxicity of L929 cells showed increased cell proliferation and cell viability for 10 wt% compared to other concentrations (Gu *et al.*, 2011b, 2010). Cui *et al.* (2019) studied the effects of HAp reinforcement on Mg-2.5 Zn alloy for the mechanical strength, degradation and cytotoxicity. The composites were prepared by the spark plasma sintering. The results showed 49% decrease in corrosion rate and 43% increase in the mechanical strength. There was no noted cytotoxicity tested for L929 fibroblast cells (Cui *et al.*, 2019). Dubey *et al.* (2019) evaluated the mechanical integrity of Mg-HAp composites after in vitro exposure to the physiological solution (SBF). Mg-3Zn matrix was reinforced with 5 wt% HAp and immersed in SBF for 14 days. The results showed that the addition of 5 HAp retained the tensile integrity of the structures by 34% and 66% of compressive strength after 14 days immersion (Dubey *et al.*, 2019). Satish *et al.* Jaiswal *et al.* (2018) reinforced Mg-3 Zn matrix with 5 wt% HAp. Addition of 5 wt% increased the CYS by 23% and reduced the corrosion rate by 42%. HAp helps in apatite layer growth More apatite layer was observed with increasing period of immersion. Apatite layer formation on 5 wt% HA

Table 12 Mechanical and corrosion properties of magnesium matrix composites

Materials	Average size of reinforcement (nm)	Grain size (μm)	Microhardness (HV)	Tensile properties			Compression properties		
				0.2% TYS (MPa)	UTS (MPa)	Failure Strain (%)	0.2% CYS (MPa)	UCS (MPa)	Failure Strain (%)
Pure Mg		16 $\pm$ 4	49 $\pm$ 2	73.5 $\pm$ 5.4	130.3 $\pm$ 4.4	13.82 $\pm$ 1.42	86 $\pm$ 1	326 $\pm$ 1	20.8 $\pm$ 1.7
Mg/0.58Ti	30–50 (DMD)	4.65 $\pm$ 1.5	54.7 $\pm$ 1.7	134 $\pm$ 7 ($\uparrow$ 82%)	190 $\pm$ 7 ($\uparrow$ 46%)	6.3 $\pm$ 0.6 ($\downarrow$ 54%)	129 $\pm$ 2 ($\uparrow$ 50%)	431 $\pm$ 8 ($\uparrow$ 32%)	17.4 $\pm$ 0.3 ($\downarrow$ 16%)
Mg/0.97Ti	30–50	2.5 $\pm$ 1.5	57.8 $\pm$ 1.45	135 $\pm$ 3 ($\uparrow$ 83%)	197 $\pm$ 8 ($\uparrow$ 51%)	8.3 $\pm$ 0.6 ($\downarrow$ 40%)	130 $\pm$ 8 ($\uparrow$ 51%)	413 $\pm$ 15 ($\uparrow$ 26%)	18.5 $\pm$ 0.6 ($\downarrow$ 11%)
Mg/1.98Ti	30–50	1.25 $\pm$ 0.25	70 $\pm$ 2	162 $\pm$ 5 ($\uparrow$ 120%)	231 $\pm$ 12 ($\uparrow$ 77%)	7.7 $\pm$ 0.1 ($\downarrow$ 44%)	120 $\pm$ 5 ($\uparrow$ 40%)	415 $\pm$ 4 ($\uparrow$ 27%)	17.7 $\pm$ 0.8 ($\downarrow$ 15%)
Pure Mg		27 $\pm$ 7	40 $\pm$ 1	116 $\pm$ 11	168 $\pm$ 10	6.1 $\pm$ 2.0			
Mg/0.3Cu	50 (PM + MW)	17 $\pm$ 5	49 $\pm$ 1	188 $\pm$ 13 ($\uparrow$ 62%)	218 $\pm$ 11 ($\uparrow$ 30%)	5.9 $\pm$ 1.1 ($\downarrow$ 3.3%)			
Mg/0.6Cu	50	15 $\pm$ 4	52 $\pm$ 2	237 $\pm$ 24 ($\uparrow$ 104%)	286 $\pm$ 8 ($\uparrow$ 70%)	5.4 $\pm$ 1.2 ($\downarrow$ 11.5%)			
Mg/1Cu	50	15 $\pm$ 4	60 $\pm$ 3	194 $\pm$ 17 ($\uparrow$ 67%)	221 $\pm$ 17 ($\uparrow$ 32%)	2.9 $\pm$ 0.4 ($\downarrow$ 52%)			
Pure Mg		23 $\pm$ 6	46 $\pm$ 3	134 $\pm$ 11	190 $\pm$ 10	4.6 $\pm$ 0.6			
Mg/0.25Al	18 (PM + TF)	17 $\pm$ 5	54 $\pm$ 1	181 $\pm$ 14 ($\uparrow$ 35%)	221 $\pm$ 15 ($\uparrow$ 16%)	4.8 $\pm$ 0.4 ($\uparrow$ 4.3%)			
Mg/0.5Al	18	17 $\pm$ 8	57 $\pm$ 1	218 $\pm$ 16 ($\uparrow$ 63%)	271 $\pm$ 11 ($\uparrow$ 43%)	6.2 $\pm$ 0.9 ($\uparrow$ 35%)			
Mg/0.75 Al	18	16 $\pm$ 7	60 $\pm$ 1	202 $\pm$ 7 ($\uparrow$ 51%)	261 $\pm$ 10 ($\uparrow$ 37%)	5.0 $\pm$ 1.6 ($\uparrow$ 8.7%)			
Mg/1 Al	18	16 $\pm$ 6	61 $\pm$ 1	185 $\pm$ 9 ($\uparrow$ 38%)	226 $\pm$ 12 ($\uparrow$ 19%)	3.3 $\pm$ 1.0 ($\downarrow$ 28%)			
Pure Mg		45 $\pm$ 2	52 $\pm$ 1.5	74 $\pm$ 5	130 $\pm$ 5	14 $\pm$ 1	55 $\pm$ 4	337 $\pm$ 1.8	18 $\pm$ 0.5
Mg/0.58TiC	30–50 (DMD)	26.9 $\pm$ 3	55 $\pm$ 1	94 $\pm$ 3 ($\uparrow$ 27%)	156 $\pm$ 3.5 ($\uparrow$ 20%)	18 $\pm$ 1.5 ($\uparrow$ 29%)	74 $\pm$ 0.5 ($\uparrow$ 35%)	329 $\pm$ 12 ($\downarrow$ 2.4%)	20.5 $\pm$ 2 ($\uparrow$ 14%)
Mg/0.97TiC	30–50	23 $\pm$ 2	57 $\pm$ 1.5	87 $\pm$ 2 ($\uparrow$ 18%)	149 $\pm$ 5 ($\uparrow$ 15%)	22 $\pm$ 0.5 ($\uparrow$ 57%)	82 $\pm$ 3.7 ($\uparrow$ 49%)	331 $\pm$ 10 ($\downarrow$ 1.8%)	17 $\pm$ 2 ($\downarrow$ 5.6%)
Mg/1.98TiC	30–50	21 $\pm$ 2	60.5 $\pm$ 2	125 $\pm$ 5 ($\uparrow$ 69%)	190 $\pm$ 14 ($\uparrow$ 46%)	20 $\pm$ 1 ($\uparrow$ 43%)	77.5 $\pm$ 3 ($\uparrow$ 41%)	340 $\pm$ 11 ($\uparrow$ 0.9%)	19 $\pm$ 2 ($\uparrow$ 5.6%)
Pure Mg			39 $\pm$ 2	125 $\pm$ 15	172 $\pm$ 12	5.8 $\pm$ 0.9			
Mg/0.35SiC	45–55 (PM + MW)		40 $\pm$ 1	132 $\pm$ 14 ($\uparrow$ 5.6%)	194 $\pm$ 11 ($\uparrow$ 13%)	6.3 $\pm$ 1.0 ($\uparrow$ 8.6%)			
Mg/0.5SiC	45–55		42 $\pm$ 1	144 $\pm$ 12 ($\uparrow$ 15%)	194 $\pm$ 10 ($\uparrow$ 13%)	7.0 $\pm$ 2.0 ($\uparrow$ 21%)			
Mg/1SiC	45–55		43 $\pm$ 2	157 $\pm$ 22 ($\uparrow$ 26%)	203 $\pm$ 22 ($\uparrow$ 18%)	7.6 $\pm$ 1.5 ($\uparrow$ 31%)			
Pure Mg		28 $\pm$ 9	48 $\pm$ 1	120 $\pm$ 9	169 $\pm$ 11	6.4 $\pm$ 0.7			
Mg/0.35B ₄ C	50 (DMD)	21 $\pm$ 5	51 $\pm$ 3	127 $\pm$ 6 ($\uparrow$ 5.8%)	202 $\pm$ 6 ($\uparrow$ 20%)	11.8 $\pm$ 1.6 ($\uparrow$ 84%)			
Mg/1.04B ₄ C	50	18 $\pm$ 9	55 $\pm$ 3	137 $\pm$ 5 ($\uparrow$ 14%)	215 $\pm$ 8 ($\uparrow$ 27%)	17.4 $\pm$ 2.0 ($\uparrow$ 171%)			
Mg/1.74B ₄ C	50	11 $\pm$ 6	57 $\pm$ 2	160 $\pm$ 2 ($\uparrow$ 33%)	240 $\pm$ 5 ($\uparrow$ 42%)	12.4 $\pm$ 1.7 ($\uparrow$ 94%)			
Pure Mg		20 $\pm$ 3	–	109 $\pm$ 09	161 $\pm$ 16	8.9 $\pm$ 1.1	93 $\pm$ 02	246 $\pm$ 23	19.4 $\pm$ 0.8
Mg/0.22B ₄ C	50 (PM + MW)	11 $\pm$ 2	–	110 $\pm$ 15 ($\uparrow$ 1%)	159 $\pm$ 14 ($\downarrow$ 1.2%)	9.9 $\pm$ 0.6 ($\uparrow$ 11%)	97 $\pm$ 04 ($\uparrow$ 4.3%)	337 $\pm$ 14 ($\uparrow$ 37%)	10.0 $\pm$ 1.6 ($\downarrow$ 48%)
Mg/0.66B ₄ C	50	10 $\pm$ 3	–	120 $\pm$ 05 ($\uparrow$ 10%)	164 $\pm$ 06 ($\uparrow$ 1.9%)	10.0 $\pm$ 0.3 ($\uparrow$ 12%)	100 $\pm$ 05 ($\uparrow$ 7.5%)	335 $\pm$ 11 ($\uparrow$ 36%)	11.8 $\pm$ 1.8 ($\downarrow$ 39%)
Mg/1.11B ₄ C	50	10 $\pm$ 2	–	82 $\pm$ 11 ($\downarrow$ 25%)	119 $\pm$ 17 ($\downarrow$ 26%)	5.5 $\pm$ 1.2 ($\downarrow$ 38%)	105 $\pm$ 03 ($\uparrow$ 13%)	331 $\pm$ 10 ($\uparrow$ 35%)	13.3 $\pm$ 1.4 ($\downarrow$ 31%)
Pure Mg	50 (PM + MW)	27 $\pm$ 7	40 $\pm$ 1	116 $\pm$ 11	168 $\pm$ 10	6.1 $\pm$ 2.0			
Mg/0.3 Al ₂ O ₃	50	–	48 $\pm$ 3	119 $\pm$ 7 ($\uparrow$ 2.6%)	175 $\pm$ 8 ($\uparrow$ 4.2%)	7.5 $\pm$ 0.2 ($\uparrow$ 23%)			
Mg/0.6 Al ₂ O ₃	50	24 $\pm$ 4	54 $\pm$ 3	130 $\pm$ 5 ($\uparrow$ 12%)	180 $\pm$ 7 ($\uparrow$ 7.1%)	7.4 $\pm$ 0.3 ($\uparrow$ 21%)			
Mg/1 Al ₂ O ₃	50	15 $\pm$ 3	60 $\pm$ 4	154 $\pm$ 5 ($\uparrow$ 33%)	213 $\pm$ 12 ($\uparrow$ 27%)	6.3 $\pm$ 0.4 ($\uparrow$ 3.3%)			
Mg/1.5 Al ₂ O ₃	50	18 $\pm$ 3	68 $\pm$ 2	148 $\pm$ 10 ($\uparrow$ 28%)	209 $\pm$ 7 ($\uparrow$ 24%)	5.6 $\pm$ 0.3 ($\downarrow$ 8.2%)			
Pure Mg		45 $\pm$ 2.4	52 $\pm$ 1.5	92 $\pm$ 5	156 $\pm$ 6	8.2 $\pm$ 0.2	57 $\pm$ 3	332 $\pm$ 10	18
Mg/0.58 TiO ₂	21 (DMD)	37 $\pm$ 3.6	58 $\pm$ 2	80 $\pm$ 2 ($\downarrow$ 13%)	128 $\pm$ 3 ($\downarrow$ 18%)	10 $\pm$ 0.5 ($\uparrow$ 22%)	78 $\pm$ 5 ($\uparrow$ 37%)	285 $\pm$ 13 ($\downarrow$ 14%)	22.6 $\pm$ 1 ($\uparrow$ 26%)
Mg/0.97 TiO ₂	21	29 $\pm$ 2	61 $\pm$ 2	97 $\pm$ 3 ($\uparrow$ 5.4%)	154 $\pm$ 7 ($\downarrow$ 1.3%)	10.8 $\pm$ 1 ($\uparrow$ 32%)	85.5 $\pm$ 2 ($\uparrow$ 49%)	278.4 $\pm$ 8 ($\downarrow$ 16%)	22.5 $\pm$ 1.5 ($\uparrow$ 25%)
Mg/1.98 TiO ₂	21	23 $\pm$ 5.5	64 $\pm$ 3	102 $\pm$ 3 ($\uparrow$ 11%)	165.5 $\pm$ 3 ($\uparrow$ 5.8%)	11.5 $\pm$ 1 ($\uparrow$ 40%)	88.3 $\pm$ 1 ($\uparrow$ 55%)	297 $\pm$ 1 ($\downarrow$ 11%)	21.9 $\pm$ 1 ($\uparrow$ 22%)
Mg/2.5 TiO ₂	21	21 $\pm$ 4	68 $\pm$ 1.5	124 $\pm$ 8.8 ($\uparrow$ 35%)	170 $\pm$ 6 ($\uparrow$ 9%)	10 $\pm$ 1 ($\uparrow$ 22%)	101 $\pm$ 9 ($\uparrow$ 77%)	305.5 $\pm$ 11 ($\downarrow$ 8%)	22 $\pm$ 2 ($\uparrow$ 22%)

Pure Mg	21 (PM + MW)	32 ± 1.5	50 ± 2	89 ± 4.5	142 ± 6	10 ± 0.3	76 ± 2	275 ± 4	20 ± 1.5
Mg/1.98 TiO ₂	21	28 ± 1.5	60 ± 1	88 ± 10	132 ± 8 (↓5%)	14.5 ± 1 (↑55%)	89.9 ± 2 (↑18%)	245 ± 8 (↓9%)	25 ± 2 (↑26%)
Mg/2.5 TiO ₂	21	25 ± 2.5	64 ± 3	91.1 ± 5 (↑3%)	134 ± 7 (↓5%)	6 ± 1 (↓30%)	81 ± 0.6 (↑6)	233 ± 6 (↓14%)	24 ± 2 (↑21%)
Pure Mg		37 ± 11	–	95 ± 8	133 ± 7	8.3 ± 2.9	66 ± 8	228 ± 7	22.2 ± 0.9
Mg/0.16ZnO	90 (DMD)	19 ± 9	–	119 ± 11 (↑25%)	204 ± 9 (↑53%)	15 ± 1.4 (↑81%)	98 ± 5 (↑48%)	284 ± 6 (↑25%)	22.3 ± 0.5
Mg/0.48ZnO	90	22 ± 10	–	131 ± 6 (↑38%)	210 ± 8 (↑58%)	16.3 ± 1.4 (↑96%)	110 ± 2 (↑67%)	308 ± 9 (↑35%)	22.5 ± 1.2
Mg/0.8ZnO	90	16 ± 7	–	147 ± 9 (↑55%)	237 ± 8 (↑78%)	11.88 ± 1.7 (↑43%)	125 ± 8 (↑89%)	345 ± 4 (↑51%)	21.7 ± 2.1
Pure Mg		49.0±8.1	40.0±0.2	97±2	173±1	7.4±0.2			
Mg/0.22 ZrO ₂	29–68 (DMD)	7.6±2.0	47.1±0.6	186±2 (↑91%)	248±4 (↑43%)	4.7±0.2 (↓36%)			
Mg/0.66 ZrO ₂	29–68	4.9±1.5	51.0±0.6	221±5 (↑127%)	271±6 (↑57%)	4.8±0.7 (↓35%)			
Mg/1.11 ZrO ₂	29–68	2.3±0.5	54.7±0.7	216±4 (↑122%)	250±6 (↑44%)	3.0±0.2 (↓59%)			
Pure Mg		25 ± 7	42.0 ± 1.6	111 ± 7.8	177 ± 10	9.0 ± 2.2	109 ± 4	284 ± 11	23 ± 3
Mg/0.3 ZrO ₂	51–65 (PM + MW)	24 ± 7	40.0 ± 1.0	84.8 ± 8.0 (↓24%)	139 ± 7.5 (↓21%)	8.1 ± 1.6 (↓10%)	109 ± 6	273 ± 13 (↓3.9%)	19 ± 1 (↓17%)
Mg/0.6 ZrO ₂	51–65	29 ± 3	41.6 ± 2.1	117 ± 11 (↑5.4%)	182 ± 14 (↑2.8%)	9.4 ± 2.7 (↑4.4%)	–	–	–
Mg/1.0 ZrO ₂	51–65	25 ± 4	42.1 ± 1.9	97.8 ± 6.3 (↓12%)	158 ± 12 (↓11%)	8.6 ± 2.2 (↓4.4%)	109 ± 5	262 ± 18 (↓7.7%)	19 ± 4 (↓17%)
Mg / (0.3 ZrO ₂ + 0.7 Cu)	ZrO ₂ (51–65 nm), Cu(25 nm)	9 ± 2	47.6 ± 1.0	196 ± 16 (↑77%)	249 ± 8 (↑40%)	8.2 ± 1.1 (↓8.9%)	124 ± 7 (↑14%)	352 ± 18 (↑24%)	12 ± 3 (↓48%)
Mg / (0.6 ZrO ₂ + 0.4 Cu)	ZrO ₂ (51–65 nm), Cu(25 nm)	11 ± 3	50±1	139 ± 22 (↑25%)	193 ± 21 (↑9%)	11.4 ± 2.9 (↑27%)	–	–	–
Pure Mg		49 ± 8	40±0	97±2	173±1	7.4±0.2			
Mg/0.22 Y ₂ O ₃	29 (DMD)	10 ± 1	51±0	218±2 (↑125%)	277±5 (↑60%)	12.7±1.3 (↑72%)			
Mg/0.66 Y ₂ O ₃	29	6 ± 1	51±0	312±4 (↑222%)	318±2 (↑84%)	6.9±1.6 (↓6.8%)			
Mg/1.11 Y ₂ O ₃	29	6 ± 2	52±1	–	205±3 (↑18%)	1.7±0.5 (↓77%)			
Pure Mg		20 ± 3	40 ± 1	134 ± 7	193 ± 2	7.5 ± 2.5			
Mg/0.2 Y ₂ O ₃	29 (PM + MW)	19 ± 3	38 ± 0	144 ± 2 (↑7.5%)	214 ± 4 (↑11%)	8.0 ± 2.8 (↑7%)			
Mg/0.7 Y ₂ O ₃	29	18 ± 3	45 ± 2	157 ± 10 (↑17%)	244 ± 1 (↑26%)	8.6 ± 1.2 (↑15%)			
Pure Mg		28±11	48±1	120±9	169±11	6.4±0.7	70±8	234±8	20.7±0.9
Mg/0.3BN	50 (DMD)	18±6	51±3	133±4 (↑11%)	193±7 (↑14%)	8.6±0.6 (↑35%)	84±9 (↑20%)	275±12 (↑18%)	18.9±0.7 (↓8.7%)
Mg/0.6BN	50	15±4	55±3	154±2 (↑29%)	223±2 (↑32%)	15.3±0.8 (↑139%)	97±3 (↑39%)	297±8 (↑27%)	
Mg/1.2BN	50	9±3	67±2	178±5 (↑48%)	255±3 (↑51%)	12.6±1.3 (↑97%)	109±4 (↑56%)	307±6 (↑31%)	17.6±2.0 (↓15%)
Pure Mg		28.94 ± 5.86	48 ± 1	136 ± 8	170 ± 7	6.1 ± 1.2	70 ± 2	250 ± 7	24.5 ± 2.7
Mg/0.29BN	50 (PM + MW)	21.42 ± 2.67	51 ± 3	127 ± 6 (↓6.6%)	192 ± 8 (↑13%)	7.8 ± 0.9 (↑28%)	88 ± 6 (↑26%)	290 ± 9 (↑16%)	20.9 ± 1.8 (↓15%)
Mg/0.86BN	50	22.15 ± 1.92	55 ± 3	142 ± 4 (↑4.4%)	200 ± 5 (↑18%)	8.6 ± 0.5 (↑41%)	108 ± 2 (↑54%)	312 ± 8 (↑25%)	19.9 ± 1.2 (↓19%)
Mg/1.44BN	50	19.43 ± 3.43	57 ± 2	145 ± 3 (↑6.6%)	217 ± 5 (↑28%)	7.2 ± 0.8 (↑18%)	115 ± 4 (↑64%)	319 ± 4 (↑28%)	19.7 ± 1.4 (↓20%)
Pure Mg		28.2 ± 7.7	41 ± 3	96 ± 6	137 ± 9	6.0 ± 3.0	51 ± 9	268 ± 16	18.9 ± 1.6
Mg/0.2AlN	75 (PM + MW)	23.8 ± 7.9	49 ± 3	102 ± 6 (↑6.3%)	159 ± 8 (↑16%)	11.0 ± 2.2 (↑83%)	65 ± 1 (↑27%)	284 ± 12 (↑6%)	19.3 ± 1.5 (↑2%)
Mg/0.4AlN	75	19.6 ± 6.2	55 ± 3	120 ± 1 (↑25%)	164 ± 3 (↑20%)	8.4 ± 0.9 (↑40%)	72 ± 5 (↑41%)	314 ± 20 (↑17%)	17.5 ± 0.6 (↓7.4%)
Mg/0.8AlN	75	19.4 ± 5.3	53 ± 8	129 ± 5 (↑34%)	176 ± 3 (↑28%)	6.3 ± 0.4 (↑5%)	71 ± 3 (↑39%)	307 ± 17 (↑15%)	18.3 ± 2.3 (↓3.2%)

Note: Gupta, M., Ling, S.N.M., 2011. Magnesium, Magnesium Alloys, and Magnesium Composites. John Wiley & Sons.

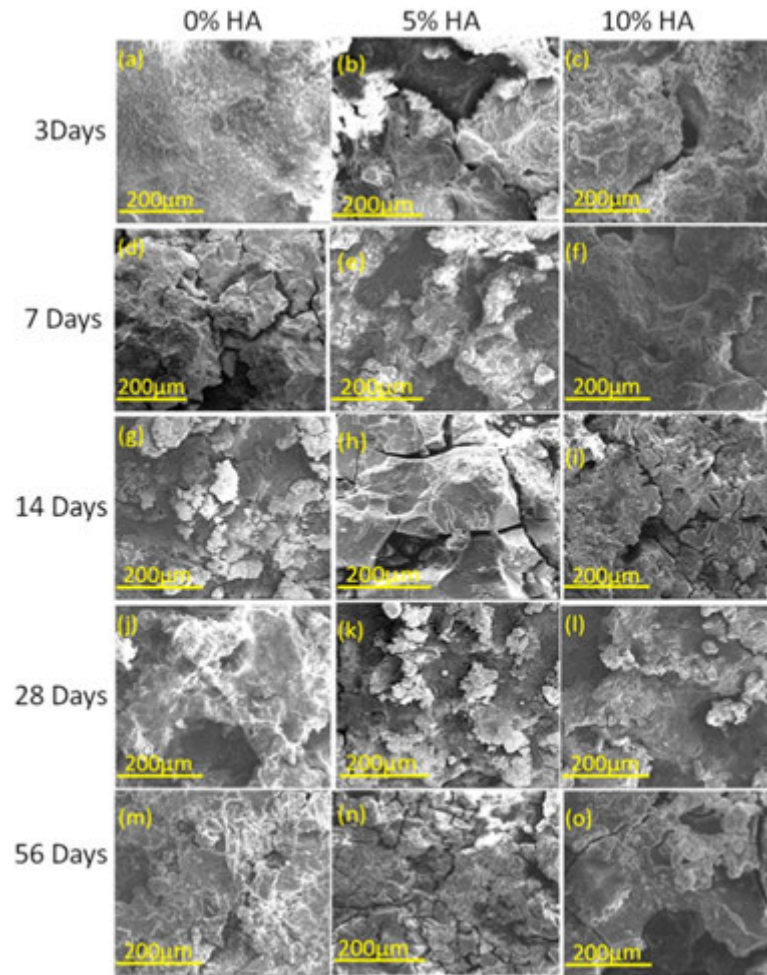


Fig. 8 SEM micrograph of composite structures immersed for (a, b, c) 3 Days, (d, e, f) 7Days, (g, h, i) 14 Days, (j, k, l) 28 Days and (m, n, o) 56 Days. Reproduced from Jaiswal, S., *et al.*, 2018. Mechanical, corrosion and biocompatibility behaviour of Mg-3Zn-HA biodegradable composites for orthopaedic fixture accessories. *Journal of the Mechanical Behavior of Biomedical Materials* 78, 442–454.

composite was higher which is the reason for lower degradation rate of 5 wt% HA composite. The in vitro cytotoxic studies showed increased cell proliferation and well-formed spindle shape cell morphology (Jaiswal *et al.*, 2018) (Fig. 8). Ramya *et al.* (2018) studied that the addition of nano HAp particles to $Mg_{66}Zn_{30}Ca_4$ metallic glass and reported increased cell viability of MG63 osteoblast like cells, marginal improvement in the mechanical properties and increased corrosion resistance of the composite (Ramya *et al.*, 2018).

DMD-Disintegrated Melt Deposition, PM-Powder Metallurgy, MW-Microwave Sintering

Mg/ β -TCP composites with 0.5, 1, 1.5% reinforcement was studied for mechanical strength and corrosion property. Addition of β -TCP increased the compressive strength by 53%, yield strength by 34% and compressive fracture strain by 22%. 1.5% β -TCP showed 70% reduction in the grain size and corrosion studies done in HBSS showed decrease in corrosion rate compared to pure magnesium (Parande *et al.*, 2016). Comparison of MgO surface modified β -TCP and unmodified β -TCP addition with Mg-3Zn-0.8Zr alloy showed increase in the compressive strength and decrease in the corrosion rates for modified β -TCP reinforcement composites. There was no significant difference in the cell viability and cell proliferation for both the composites (Zheng *et al.*, 2017).

Mg reinforced with 20 vol% SiO_2 showed reduced grain size and decreased corrosion rate and good mechanical strength (Parande *et al.*, 2016). Mg reinforced with hollow nano SiO_2 particles of concentration 0.5, 1, 1.5% showed decreased grain size and increased mechanical strength. The in vitro cytotoxicity results showed increased cell proliferation and cell viability for 0.5% and 1% SiO_2 reinforcement. Addition of SiO_2 reduced the corrosion rate compare to pure Mg.

Conclusions

A biomaterial is any substance (other than drugs), natural or synthetic, that treats, augments, or replaces any tissue, organ, and body function. Biomaterial selection is one of the most challenging issues due to crucial requirements and biocompatibility, so it has been of major interest to material designers in recent years. This review of metal matrix composites targeting biomedical applications has attempted to demonstrate the very significant progress that has been made with the use of advanced materials such as magnesium within the human body. The present study reviewed the currently used metal matrix composites for various biomedical applications. Metals are susceptible to degradation by corrosion, a process that can release by-products that may cause adverse biological responses. Ceramics are attractive as biological implants for their biocompatibility. The studies, for example, have shown that alumina with high mechanical strength show minimal or no tissue reaction, nontoxic to tissues and blood compatibility tests were also satisfactory. Carbon with similar mechanical properties of bone is an exciting candidate, for it elicits blood compatibility, no tissue reaction and nontoxicity to cells. The integration of biocompatible metals with ceramics and non-metals such as mentioned above can lead to superior implants with enhanced performance. Innovations in the composite material design and fabrication processes are raising the possibility of realizing implants with improved performance in very near future. However, for successful applications, surgeons must be convinced with the long term durability and reliability of composite biomaterials. In the past, success of materials in biomedical applications was not so much the outcome of meticulous selection based on biocompatibility criteria but rather the result of serendipity, continuous refinement in fabrication technology, and advances in material surface treatment. In the present and future, selection of a biomaterial for a specific application must be based on several criteria. Biocompatibility is the paramount criterion that must be met by every biomaterial. Medical research continues to explore new scientific frontiers for diagnosing, treating, curing, and preventing diseases at the molecular/genetic level. This review should be of value to researchers who are interested in the state of the art of biomaterial development and selection. In the future, we can anticipate seeing novel composite biomaterials that will enhance the comfort levels of patient. Therefore, it is vital to accentuate the need for precise studies that will determine the behavior of these novel materials prior to their clinical use and determining an approach to improve the biocompatibility (i.e., biological reactions) that occur instantly after implantation. However, close alliance between surgeons, biologists and engineers is vital in order to attain success with the challenging future of joint replacements.

References

- Aherwar, A., Singh, A.K., Patnaik, A., 2016. Cobalt based alloy: A better choice biomaterial for hip implants. *Trends in Biomaterials & Artificial Organs* 30 (1), 1–10.
- Albrektsson, T., Berglundh, T., Lindhe, J., Karring, T., Lang, N.P., 2003. *Clinical Periodontology and Implant Dentistry*. Oxford: Blackwell Munksgaard, A Blackwell Publishing Company.
- Al-Samman, T., Li, X., 2011. Sheet texture modification in magnesium-based alloys by selective rare earth alloying. *Materials Science and Engineering: A* 528 (10–11), 3809–3822.
- Alvarado, J., Maldonado, R., Marxuach, J., Otero, R., 2003. Biomechanics of hip and knee prostheses. In *Applications of Engineering Mechanics in Medicine*. GED—University of Puerto Rico Mayaguez. pp. 1–20.
- Aral, H., Vecchio-Sadus, A., 2008. Toxicity of lithium to humans and the environment – A literature review. *Ecotoxicology and Environmental Safety* 70 (3), 349–356.
- ASTMF, 1981. *Standard Specification for Unalloyed Titanium for Surgical Implant Applications*. American Society for Testing and Materials, Philadelphia, PA.
- ASTMF136, 2013. *Standard Specification for Wrought Titanium-6Aluminum-4Vanadium ELI (Extra Low Interstitial) Alloy for Surgical Implant Applications (UNS R56401)*.
- Atkins, G., et al., 2009. Strontium ranelate treatment of human primary osteoblasts promotes an osteocyte-like phenotype while eliciting an osteoprotegerin response. *Osteoporosis International* 20 (4), 653–664.
- Avolio, R., et al., 2016. Pure titanium particle loaded nanocomposites: study on the polymer/filler interface and hMSC biocompatibility. *Journal of Materials Science: Materials in Medicine* 27 (10), 153.
- Bakhsheshi-Rad, H., et al., 2017. Thermal characteristics, mechanical properties, in vitro degradation and cytotoxicity of novel biodegradable Zn–Al–Mg and Zn–Al–Mg–xBi alloys. *Acta Metallurgica Sinica (English Letters)* 30 (3), 201–211.
- Bandyopadhyay, A., et al., 2016. Calcium phosphate–titanium composites for articulating surfaces of load-bearing implants. *Journal of the mechanical behavior of biomedical materials* 57, 280–288.
- Basar, B., et al., 2010. Improvements in microstructural, mechanical, and biocompatibility properties of nano-sized hydroxyapatites doped with yttrium and fluoride. *Ceramics International* 36 (5), 1633–1643.
- Bayani, H., Saebnoori, E., 2009. Effect of rare earth elements addition on thermal fatigue behaviors of AZ91 magnesium alloy. *Journal of Rare Earths* 27 (2), 255–258.
- Bensmann, G., 1999. An attempt to assess material suitability taking the example of hip endoprostheses. *Materialwissenschaft und Werkstofftechnik: Entwicklung, Fertigung, Prüfung, Eigenschaften und Anwendungen technischer Werkstoffe* 30 (12), 733–745.
- Birbilis, N., et al., 2011. A combined neural network and mechanistic approach for the prediction of corrosion rate and yield strength of magnesium–rare earth alloys. *Corrosion Science* 53 (1), 168–176.
- Bitar, D., Parvizi, J., 2015. Biological response to prosthetic debris. *World Journal of Orthopedics* 6 (2), 172.
- Bock, N.A., Paiva, F.F., Silva, A.C., 2008. Fractionated manganese-enhanced MRI. *NMR in Biomedicine* 21 (5), 473–478.
- Bommala, V.K., Krishna, M.G., Rao, C.T., 2018. Magnesium matrix composites for biomedical applications: A review. *Journal of Magnesium and Alloys*.
- Bornapour, M., et al., 2013. Biocompatibility and biodegradability of Mg–Sr alloys: The formation of Sr-substituted hydroxyapatite. *Acta Biomaterialia* 9 (2), 5319–5330.
- Bowen, P.K., et al., 2016. Biodegradable metals for cardiovascular stents: From clinical concerns to recent Zn-alloys. *Advanced Healthcare Materials* 5 (10), 1121–1140.
- Brandão-Neto, J., et al., 1995. The essential role of zinc in growth. *Nutrition Research* 15 (3), 335–358.
- Breme, J., Eisenbarth, E., Biehl, V., 2002. Titanlegierungen in der Medizintechnik. *Titan und Titanlegierungen*. 431–462.
- Bruce, D.W., Hietbrink, B.E., DuBois, K.P., 1963. The acute mammalian toxicity of rare earth nitrates and oxides. *Toxicology and Applied Pharmacology* 5 (6), 750–759.
- Carter, C., 2010. Familial and late-onset alzheimer's disease: Evidence for an auto-immune component triggered by viral, microbial and allergen antigens with homology to beta-amyloid and APP mutant peptides. *Nature Precedings* 1.4662.
- Cases, N., 2005. Macrophagic myofasciitis associated with vaccine-derived aluminium. *The Medical Journal of Australia* 183 (3), 145–146.

- Chen, D., *et al.*, 2011. Biocompatibility of magnesium-zinc alloy in biodegradable orthopedic implants. *International Journal of Molecular Medicine* 28 (3), 343–348.
- Chen, Q., Zhu, C., Thouas, G.A., 2012. Progress and challenges in biomaterials used for bone tissue engineering: Bioactive glasses and elastomeric composites. *Progress in Biomaterials* 1 (1), 2.
- Chen, Y., *et al.*, 2005. Nano neodymium oxide induces massive vacuolization and autophagic cell death in non-small cell lung cancer NCI-H460 cells. *Biochemical and Biophysical Research Communications* 337 (1), 52–60.
- Chen, Y., *et al.*, 2010. Microstructure evolution of commercial pure titanium during equal channel angular pressing. *Materials Science and Engineering: A* 527 (3), 789–796.
- Christensen, F.B., *et al.*, 2000. Titanium-alloy enhances bone-pedicle screw fixation: Mechanical and histomorphometrical results of titanium-alloy versus stainless steel. *European Spine Journal* 9 (2), 97–103.
- Coleman, J.E., 1992. Zinc proteins: enzymes, storage proteins, transcription factors, and replication proteins. *Annual Review of Biochemistry* 61 (1), 897–946.
- Comin, R., *et al.*, 2017. Titanium-hydroxyapatite composites sintered at low temperature for tissue engineering: In vitro cell support and biocompatibility. *Journal of Applied Biomaterials & Functional Materials* 15 (2), 176–183.
- Cui, Z., *et al.*, 2019. Effect of nano-HA content on the mechanical properties, degradation and biocompatible behavior of Mg-Zn/HA composite prepared by spark plasma sintering. *Materials Characterization* 151, 620–631.
- Daley, B., *et al.*, 2004. Wear debris from hip or knee replacements causes chromosomal damage in human cells in tissue culture. *The Journal of Bone and Joint Surgery* 86 (4), 598–606.
- Darrah, T.H., *et al.*, 2009. Incorporation of excess gadolinium into human bone from medical contrast agents. *Metallomics* 1 (6), 479–488.
- Daugaard, H., *et al.*, 2010. The effect on bone growth enhancement of implant coatings with hydroxyapatite and collagen deposited electrochemically and by plasma spray. *Journal of Biomedical Materials Research Part A: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials* 92 (3), 913–921.
- Davis, K.G., Marras, W.S., Waters, T.R., 1998. Evaluation of spinal loading during lowering and lifting. *Clinical Biomechanics* 13 (3), 141–152.
- Del Campo, R., *et al.*, 2014. Mechanical properties and corrosion behavior of Mg–HAP composites. *Journal of the Mechanical Behavior of Biomedical Materials* 39, 238–246.
- Delongae, J., *et al.*, 1983. Toxicity and pharmacokinetics of zirconium oxychloride in mice and rats. *Journal de Pharmacologie* 14 (4), 437–447.
- Dezfuli, S.N., *et al.*, 2017. Advanced bredigite-containing magnesium-matrix composites for biodegradable bone implant applications. *Materials Science and Engineering: C* 79, 647–660.
- Ding, D., Roth, J., Salvi, R., 2011. Manganese is toxic to spiral ganglion neurons and hair cells in vitro. *Neurotoxicology* 32 (2), 233–241.
- Ding, P., *et al.*, 2019. In vitro and in vivo biocompatibility of Mg–Zn–Ca alloy operative clip. *Bioactive Materials* 4, 236–244.
- Ding, Y., *et al.*, 2014. Effects of alloying elements on the corrosion behavior and biocompatibility of biodegradable magnesium alloys: A review. *Journal of Materials Chemistry B* 2 (14), 1912–1933.
- Disegi, J., 1993. Titanium-6% Aluminum-7% Niobium Implant Material. Paoli, PA: Synthes.
- Disegi, J., Eschbach, L., 2000. Stainless steel in bone surgery. *Injury* 31, D2–D6.
- Driscoll, P., 2009. Materials Used in Stent Construction. Biddeford, ME: MedMarket Diligence, LLC.
- Dubey, A., Jaiswal, S., Lahiri, D., 2019. Mechanical integrity of biodegradable Mg–HA composite during in vitro exposure. *Journal of Materials Engineering and Performance* 28 (2), 800–809.
- Ducheyne, P., Kohn, D., 1998. *Materials Science and Technology – A Comprehensive Treatment, Medical and Dental Materials*. 14. Weinheim: Wiley, pp. 39–41.
- Ebenezer, V., *et al.*, 2015. Immediate placement of endosseous implants into the extraction sockets. *Journal of Pharmacy & Bioallied Sciences* 7 (Suppl. 1), S234.
- Eliaz, N., Metoki, N., 2017. Calcium phosphate bioceramics: a review of their history, structure, properties, coating technologies and biomedical applications. *Materials* 10 (4), 334.
- Erikson, K.M., *et al.*, 2005. Interactions between excessive manganese exposures and dietary iron-deficiency in neurodegeneration. *Environmental Toxicology and Pharmacology* 19 (3), 415–421.
- Faria, A.C., *et al.*, 2008. In vitro cytotoxicity of dental alloys and cpTi obtained by casting. *Journal of Biomedical Materials Research Part B: Applied Biomaterials: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials* 85 (2), 504–508.
- Feng, Q., *et al.*, 2013. Characterization and in vivo evaluation of a bio-corrodible nitrided iron stent. *Journal of Materials Science: Materials in Medicine* 24 (3), 713–724.
- Ferrante, M., *et al.*, 2013. *Health Effects of Metals and Related Substances in Drinking Water*. IWA Publishing.
- Feser, K., *et al.*, 2011. Effects of degradable Mg–Ca alloys on dendritic cell function. *Journal of Biomaterials Applications* 25 (7), 685–697.
- Feyerabend, F., *et al.*, 2010. Evaluation of short-term effects of rare earth and other elements used in magnesium alloys on primary cells and cell lines. *Acta Biomaterialia* 6 (5), 1834–1842.
- Fosmire, G.J., 1990. Zinc toxicity. *The American Journal of Clinical Nutrition* 51 (2), 225–227.
- Gasser, B., Eschbach, L., Biehl, V., 2000. Metallische Implantatwerkstoffe: Reintitan und Titanlegierungen. *Review of Managerial Science* 16, 7–11.
- Geetha, M., *et al.*, 2009. Ti based biomaterials, the ultimate choice for orthopaedic implants – A review. *Progress in Materials Science* 54 (3), 397–425.
- Giles, J.J., Bannigan, J.G., 2006. Teratogenic and developmental effects of lithium. *Current Pharmaceutical Design* 12 (12), 1531–1541.
- Goh, C., *et al.*, 2005. Development of novel carbon nanotube reinforced magnesium nanocomposites using the powder metallurgy technique. *Nanotechnology* 17 (1), 7.
- Gotman, I., 1997. Characteristics of metals used in implants. *Journal of Endourology* 11 (6), 383–389.
- Gu, X., *et al.*, 2009. In vitro corrosion and biocompatibility of binary magnesium alloys. *Biomaterials* 30 (4), 484–498.
- Gu, X., *et al.*, 2010. Microstructure, biocorrosion and cytotoxicity evaluations of rapid solidified Mg–3Ca alloy ribbons as a biodegradable material. *Biomedical Materials* 5 (3), 035013.
- Gu, X., *et al.*, 2011a. In vitro degradation performance and biological response of a Mg–Zn–Zr alloy. *Materials Science and Engineering: B* 176 (20), 1778–1784.
- Gu, X., *et al.*, 2011b. Corrosion resistance and surface biocompatibility of a microarc oxidation coating on a Mg–Ca alloy. *Acta Biomaterialia* 7 (4), 1880–1889.
- Guillory, R.J., *et al.*, 2016. Corrosion characteristics dictate the long-term inflammatory profile of degradable zinc arterial implants. *ACS Biomaterials Science & Engineering* 2 (12), 2355–2364.
- Guillory II, R.J., *et al.*, 2019. In vitro corrosion and in vivo response to zinc implants with electropolished and anodized surfaces. *ACS Applied Materials & Interfaces* 11 (12), 19884–19893.
- Guimaraes, Z.A., *et al.*, 2017. A novel porous diamond-titanium biomaterial: Structure, microstructure, physico-mechanical properties and biocompatibility. *Anais da Academia Brasileira de Ciências* 89 (4), 3111–3121.
- Gürsel, F., *et al.*, 2012. Effect of Garcinia cambogia extract on body weight gain, feed intake and feed conversion ratio, and serum non-esterified fatty acids and C-reactive protein levels in rats fed with atherogenic diet. *Biological Trace Element Research* 148 (3), 378–382.
- Ha, S.-W., 2008. *EW: Medizintechnik-Life Science Engineering*. Berlin Heidelberg: Springer-Verlag.
- Habibnejad-Korayem, M., Mahmudi, R., Poole, W.J., 2009. Enhanced properties of Mg-based nano-composites reinforced with Al₂O₃ nano-particles. *Materials Science and Engineering: A* 519 (1–2), 198–203.
- Hatfield, W., 1931. Rustless steels as applied to automobiles and aircraft. *Proceedings of the Institution of Automobile Engineers* 25 (2), 285–304.
- Haude, M., *et al.*, 2013. Safety and performance of the drug-eluting absorbable metal scaffold (DREAMS) in patients with de-novo coronary lesions: 12 month results of the prospective, multicentre, first-in-man BIOSOLVE-I trial. *The Lancet* 381 (9869), 836–844.
- Heary, R.F., *et al.*, 2017. Elastic modulus in the selection of interbody implants. *Journal of Spine Surgery* 3 (2), 163.

- Heiden, M., Walker, E., Stanciu, L., 2015. Magnesium, iron and zinc alloys, the trifecta of bioresorbable orthopaedic and vascular implantation—a review. *Journal of Biotechnology & Biomaterials* 5 (2), 1.
- Heuberger, R., 2009. Roughness measurements on the groove of threads of locking screws star drive® after different treatments. *RMS Report* 9, 1–6.
- Hirano, S., *et al.*, 1993. Metabolism and toxicity of intravenously injected yttrium chloride in rats. *Toxicology and Applied Pharmacology* 121 (2), 224–232.
- Hong, D., *et al.*, 2016. Binder-jetting 3D printing and alloy development of new biodegradable Fe-Mn-Ca/Mg alloys. *Acta Biomaterialia* 45, 375–386.
- Huan, Z., *et al.*, 2010. In vitro degradation behavior and cytocompatibility of Mg–Zn–Zr alloys. *Journal of Materials Science: Materials in Medicine* 21 (9), 2623–2635.
- Huan, Z., *et al.*, 2016. Substantial enhancement of corrosion resistance and bioactivity of magnesium by incorporating calcium silicate particles. *RSC Advances* 6 (53), 47897–47906.
- Huang, Y., *et al.*, 2015. Fabrication and characterization of a biodegradable Mg–2Zn–0.5Ca/1 β -TCP composite. *Materials Science and Engineering: C* 54, 120–132.
- Ilich, J.Z., Kerstetter, J.E., 2000. Nutrition in bone health revisited: A story beyond calcium. *Journal of the American College of Nutrition* 19 (6), 715–737.
- Izumi, S., Yamasaki, M., Kawamura, Y., 2009. Relation between corrosion behavior and microstructure of Mg–Zn–Y alloys prepared by rapid solidification at various cooling rates. *Corrosion Science* 51 (2), 395–402.
- Jaiswal, S., *et al.*, 2018. Mechanical, corrosion and biocompatibility behaviour of Mg–3Zn–HA biodegradable composites for orthopaedic fixture accessories. *Journal of the Mechanical Behavior of Biomedical Materials* 78, 442–454.
- Jin, H., *et al.*, 2018. Novel high-strength, low-alloys Zn–Mg (< 0.1 wt% Mg) and their arterial biodegradation. *Materials Science and Engineering: C* 84, 67–79.
- Johnson, J.R.K., Riechmann, G.C., 1968. Normal serum calcium levels by atomic absorption spectroscopy. *Clinical Chemistry* 14 (12), 1218–1225.
- Jung, J.Y., *et al.*, 2012. In vivo corrosion mechanism by elemental interdiffusion of biodegradable Mg–Ca alloy. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 100 (8), 2251–2260.
- Kawagoe, M., *et al.*, 2005. Orally administrated rare earth element cerium induces metallothionein synthesis and increases glutathione in the mouse liver. *Life Sciences* 77 (8), 922–937.
- Keegan, G.M., Learmonth, I.D., Case, C., 2008. A systematic comparison of the actual, potential, and theoretical health effects of cobalt and chromium exposures from industry and surgical implants. *Critical Reviews in Toxicology* 38 (8), 645–674.
- Keith, S.J.D., Rosemond, Z., Ingerman, L., Chapell, L., 2008. Toxicological Profile for Aluminium. US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry.
- Khalajabadi, S.Z., *et al.*, 2015. Microstructural characterization, biocorrosion evaluation and mechanical properties of nanostructured ZnO and Si/ZnO coated Mg/HA/TiO₂/MgO nanocomposites. *Surface and Coatings Technology* 277, 30–43.
- Kiellerich, S., *et al.*, 1980. Determination of zinc in serum and urine by atomic absorption spectrophotometry; relationship between serum levels of zinc and proteins in 104 normal subjects. *Clinica Chimica Acta* 105 (2), 231–239.
- Kirkland, N., *et al.*, 2010. A survey of bio-corrosion rates of magnesium alloys. *Corrosion Science* 52 (2), 287–291.
- Kopova, I., *et al.*, 2016. Newly developed Ti–Nb–Zr–Ta–Si–Fe biomedical beta titanium alloys with increased strength and enhanced biocompatibility. *Materials Science and Engineering: C* 60, 230–238.
- Kowalski, K., Nowak, M., Jurczyk, M., 2016. Mechanical and corrosion properties of magnesium–bioceramic nanocomposites. *Archives of Metallurgy and Materials* 61 (3), 1437–1440.
- Kraus, T., *et al.*, 2012. Magnesium alloys for temporary implants in osteosynthesis: In vivo studies of their degradation and interaction with bone. *Acta Biomaterialia* 8 (3), 1230–1238.
- Kraus, T., *et al.*, 2014. Biodegradable Fe-based alloys for use in osteosynthesis: Outcome of an in vivo study after 52 weeks. *Acta biomaterialia* 10 (7), 3346–3353.
- Krewski, D., *et al.*, 2007. Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide. *Journal of Toxicology and Environmental Health, Part B* 10 (S1), 1–269.
- Krones, C.J., *et al.*, 2005. Effect of zinc pretreatment on pulmonary endothelial cells in vitro and pulmonary function in a porcine model of endotoxemia. *Journal of Surgical Research* 123 (2), 251–256.
- Kuwahara, H., *et al.*, 2000. Surface reaction of magnesium in Hank's solutions. *Materials Science Forum*. 349–358.
- Laing, P., 1979. Clinical experience with prosthetic materials: Historical perspectives, current problems, and future directions. In: Syrett, B., Acharya, A. (Eds.), *Corrosion and Degradation of Implant Materials*. ASTM International, pp. 199–211.
- Lastra, M.D., *et al.*, 2001. Zinc intervention on macrophages and lymphocytes response. *Journal of Trace Elements in Medicine and Biology* 15 (1), 5–10.
- Legeros, R.Z., Craig, R.G., 1993. Strategies to affect bone remodeling: Osteointegration. *Journal of Bone and Mineral Research* 8 (S2), S583–S596.
- Li, N., Zheng, Y., 2013. Novel magnesium alloys developed for biomedical application: A review. *Journal of Materials Science & Technology* 29 (6), 489–502.
- Li, S., *et al.*, 2004. Wear characteristics of Ti–Nb–Ta–Zr and Ti–6Al–4V alloys for biomedical applications. *Wear* 257 (9–10), 869–876.
- Li, Y., *et al.*, 2011. Biodegradable Mg–Zr–Ca alloys for bone implant materials. In *Advanced Materials And Processing 2010*. World Scientific, pp. 9–12.
- Li, Y., *et al.*, 2012. Mg–Zr–Sr alloys as biodegradable implant materials. *Acta Biomaterialia* 8 (8), 3177–3188.
- Li, Y., *et al.*, 2014. New developments of Ti-based alloys for biomedical applications. *Materials* 7 (3), 1709–1800.
- Li, Y.C., *et al.*, 2010. Biodegradable Mg–Ca and Mg–Ca–Y alloys for regenerative medicine. *Materials Science Forum*. 2192–2195.
- Li, Z., *et al.*, 2008. The development of binary Mg–Ca alloys for use as biodegradable materials within bone. *Biomaterials* 29 (10), 1329–1344.
- Liu, D., *et al.*, 2017. The hot deformation behavior and microstructure evolution of HA/Mg–3Zn–0.8 Zr composites for biomedical application. *Materials Science and Engineering: C* 77, 690–697.
- Liu, R., *et al.*, 2019. Development of Fe-based bulk metallic glass composite as biodegradable metal. *Materials Letters* 247, 185–188.
- Liu, Y., *et al.*, 2015a. Powder metallurgical low-modulus Ti–Mg alloys for biomedical applications. *Materials Science and Engineering: C* 56, 241–250.
- Liu, Y.-C., *et al.*, 2015b. Corrosion degradation behavior of Mg–Ca alloy with high Ca content in SBF. *Transactions of Nonferrous Metals Society of China* 25 (10), 3339–3347.
- Lonerich, H., *et al.*, 1991. Analysis of the drinking water of mothers of neural tube defect infants and of normal infants for 14 selected trace elements by inductively coupled plasma-mass spectrometry (ICP-MS). *Canadian Journal of Applied Spectroscopy* 36 (1), 15–21.
- Loos, A., *et al.*, 2007. In vitro and in vivo biocompatibility testing of absorbable metal stents. In *Macromolecular Symposia*. Wiley.
- Lopez, I., *et al.*, 2009. The calcimimetic AMG 641 accelerates regression of extraosseous calcification in uremic rats. *American Journal of Physiology-Renal Physiology* 296 (6), F1376–F1385.
- Lu, J., *et al.*, 2002. The biodegradation mechanism of calcium phosphate biomaterials in bone. *Journal of Biomedical Materials Research: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials* 63 (4), 408–412.
- Ma, J., *et al.*, 2016. Bio-adaption between magnesium alloy stent and the blood vessel: A review. *Journal of Materials Science & Technology* 32 (9), 815–826.
- Ma, J., Zhao, N., Zhu, D., 2015. Endothelial cellular responses to biodegradable metal zinc. *ACS Biomaterials Science & Engineering* 1 (11), 1174–1182.
- Makkar, P., *et al.*, 2018. In vitro and in vivo assessment of biomedical Mg–Ca alloys for bone implant applications. *Journal of Applied Biomaterials & Functional Materials* 16 (3), 126–136.
- Mandal, S., *et al.*, 2019. Fe–Mn–Cu alloy as biodegradable material with enhanced antimicrobial properties. *Materials Letters* 237, 323–327.
- Marie, P.J., 2005. Strontium as therapy for osteoporosis. *Current opinion in Pharmacology* 5 (6), 633–636.
- Marti, A., 2000. Cobalt-base alloys used in bone surgery. *Injury* 31, D18–D21.

- Marti, A., Gasser, B., Mathys, R., 2000. Metallische Implantatwerkstoffe. über Kobaltbasislegierungen, die Festigkeit und Verschleissproblematik. *Review of Managerial Science* 16, 12–15.
- Mayer, O., 1931. Die ursache der knochenneubildung bei der otosklerose. *Acta Oto-Laryngologica* 15 (1), 35–73.
- McBride, M., *et al.*, 1989. Evaluation of antibacterial sensitivity testing methods for methicillin-resistant *Staphylococcus aureus* in a dermatology outpatient population. *Southern Medical Journal* 82 (2), 165–168.
- Meenashisundaram, G.K., *et al.*, 2015. Development of high performance Mg–TiO₂ nanocomposites targeting for biomedical/structural applications. *Materials & Design* 65, 104–114.
- Moghaddam, N.S., *et al.*, 2016. Three dimensional printing of stiffness-tuned, nitinol skeletal fixation hardware with an example of mandibular segmental defect repair. *Procedia CIRP* 49, 45–50.
- Mohamed, A., El-Aziz, A.M., Breiteringer, H.-G., 2019. Study of the degradation behavior and the biocompatibility of Mg–0.8 Ca alloy for orthopedic implant applications. *Journal of Magnesium and Alloys* 7 (2), 249–257.
- Morais, J.M., Papadimitrakopoulos, F., Burgess, D.J., 2010. Biomaterials/tissue interactions: Possible solutions to overcome foreign body response. *The AAPS Journal* 12 (2), 188–196.
- Morin, J., *et al.*, 2017. Graphene transfer to 3-dimensional surfaces: A vacuum-assisted dry transfer method. *2D Materials* 4 (2), 025060.
- Murni, N., *et al.*, 2015. Cytotoxicity evaluation of biodegradable Zn–3Mg alloy toward normal human osteoblast cells. *Materials Science and Engineering: C* 49, 560–566.
- Nakamura, Y., *et al.*, 1997. Differences in behavior among the chlorides of seven rare earth elements administered intravenously to rats. *Toxicological Sciences* 37 (2), 106–116.
- Navarro, M., *et al.*, 2008. Biomaterials in orthopaedics. *Journal of the Royal Society Interface* 5 (27), 1137–1158.
- Naveau, B., 2004. Strontium: A new treatment for osteoporosis. *Joint, Bone, Spine: Revue du Rhumatisme* 71 (4), 261–263.
- Nayak, S., *et al.*, 2016. Strengthening of Mg based alloy through grain refinement for orthopaedic application. *Journal of the Mechanical Behavior of Biomedical Materials* 59, 57–70.
- Nielsen, S.P., 2004. The biological role of strontium. *Bone* 35 (3), 583–588.
- Niinomi, M., 2008. Metallic biomaterials. *Journal of Artificial Organs* 11 (3), 105.
- Ortolani, A., *et al.*, 2016. The prospective opportunities offered by magnetic scaffolds for bone tissue engineering: A review. *Joints* 4 (04), 228–235.
- Pailat, S.R., Dahotre, N.B., 2009. Calcium phosphate coatings for bio-implant applications: Materials, performance factors, and methodologies. *Materials Science and Engineering: R: Reports* 66 (1–3), 1–70.
- Parande, G., *et al.*, 2016. Enhancing the hardness/compression/damping response of magnesium by reinforcing with biocompatible silica nanoparticles. *International Journal of Materials Research* 107 (12), 1091–1099.
- Pavón, J.J., *et al.*, 2019. Balancing biofunctional and biomechanical properties using porous titanium reinforced by carbon nanotubes. *Journal of Biomedical Materials Research Part A* 107 (4), 719–731.
- Peuster, M., *et al.*, 2001. A novel approach to temporary stenting: Degradable cardiovascular stents produced from corrodible metal—results 6–18 months after implantation into New Zealand white rabbits. *Heart* 86 (5), 563–569.
- Peuster, M., *et al.*, 2006. Long-term biocompatibility of a corrodible peripheral iron stent in the porcine descending aorta. *Biomaterials* 27 (28), 4955–4962.
- Pierson, D., *et al.*, 2012. A simplified in vivo approach for evaluating the bioabsorbable behavior of candidate stent materials. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 100 (1), 58–67.
- Pippi, R., 2017. Post-surgical clinical monitoring of soft tissue wound healing in periodontal and implant surgery. *International Journal of Medical Sciences* 14 (8), 721.
- Pogossova, M., *et al.*, 2013. Synthesis, structural features, and color of calcium-yttrium hydroxyapatite with copper ions in hexagonal channels. *Russian Journal of Inorganic Chemistry* 58 (4), 381–386.
- Poinern, G.E.J., Brundavanam, S., Fawcett, D., 2012. Biomedical magnesium alloys: A review of material properties, surface modifications and potential as a biodegradable orthopaedic implant. *American Journal of Biomedical Engineering* 2 (6), 218–240.
- Post, J.I., Eibl, J.K., Ross, G.M., 2008. Zinc induces motor neuron death via a selective inhibition of brain-derived neurotrophic factor activity. *Amyotrophic Lateral Sclerosis* 9 (3), 149–155.
- Prasad, K., *et al.*, 2017. Metallic biomaterials: Current challenges and opportunities. *Materials* 10 (8), 884.
- Prasadh, S., *et al.*, 2019a. The potential of magnesium based materials in mandibular reconstruction. *Metals* 9 (3), 302.
- Prasadh, S., *et al.*, 2019b. Bioresorbable nano-hydroxyapatite reinforced magnesium alloplastic bone substitute for biomedical applications: A study. In: Srivatsan, T.S., Gupta, M. (Eds.), *Nanocomposites VI: Nanoscience and Nanotechnology in Advanced Composites*. Springer, pp. 71–82.
- Prasadh, S., *et al.*, 2020. Biomechanics of alloplastic mandible reconstruction using biomaterials: The effect of implant design on stress concentration influences choice of material. *Journal of the Mechanical Behavior of Biomedical Materials* 103.103548.
- Prasadh, S., Wong, R.C.W., 2018. Unraveling the mechanical strength of biomaterials used as a bone scaffold in oral and maxillofacial defects. *Oral Science International* 15 (2), 48–55.
- Puleo, D., Nanci, A., 1999. Understanding and controlling the bone–implant interface. *Biomaterials* 20 (23–24), 2311–2321.
- Ramya, M., *et al.*, 2018. Hydroxyapatite particle (HAp) reinforced biodegradable Mg–Zn–Ca metallic glass composite for bio-implant applications. *Biomedical Physics & Engineering Express* 4 (2), 025039.
- Razavi, M., Fathi, M., Meratian, M., 2010. Microstructure, mechanical properties and bio-corrosion evaluation of biodegradable AZ91–FA nanocomposites for biomedical applications. *Materials Science and Engineering: A* 527 (26), 6938–6944.
- Ren, T., *et al.*, 2019. Evaluation of as-extruded ternary Zn–Mg–Zr alloys for biomedical implantation material: In vitro and in vivo behavior. *Materials and Corrosion* 70 (6), 1056–1070.
- Renkema, K.Y., *et al.*, 2008. Calcium and phosphate homeostasis: Concerted interplay of new regulators. *Annals of Medicine* 40 (2), 82–91.
- Roney, N., *et al.*, 2006. ATSDR evaluation of the health effects of zinc and relevance to public health. *Toxicology and Industrial Health* 22 (10), 423–493.
- Rushing, G.D., *et al.*, 2007. When it is not an infection: metal allergy after the Nuss procedure for repair of pectus excavatum. *Journal of Pediatric Surgery* 42 (1), 93–97.
- Scalbert, A., *et al.*, 2002. Absorption and metabolism of polyphenols in the gut and impact on health. *Biomedicine & Pharmacotherapy* 56 (6), 276–282.
- Schrand, A.M., *et al.*, 2007. Differential biocompatibility of carbon nanotubes and nanodiamonds. *Diamond and Related Materials* 16 (12), 2118–2123.
- Shapira, L., *et al.*, 2009. Effect of a niobium-containing titanium alloy on osteoblast behavior in culture. *Clinical Oral Implants Research* 20 (6), 578–582.
- Shim, M., *et al.*, 2002. Functionalization of carbon nanotubes for biocompatibility and biomolecular recognition. *Nano Letters* 2 (4), 285–288.
- Silva, H., Schneider, S., Neto, C.M., 2004. Study of nontoxic aluminum and vanadium-free titanium alloys for biomedical applications. *Materials Science and Engineering: C* 24 (5), 679–682.
- Smart, S., *et al.*, 2006. The biocompatibility of carbon nanotubes. *Carbon* 44 (6), 1034–1047.
- Song, G., Shayan, A., 1998. Corrosion of Steel in Concrete: Causes, Detection and Prediction: A State-of-the-Art Review. NIS. pp. 53–77.
- Song, W., *et al.*, 2009. The study on the degradation and mineralization mechanism of ion-doped calcium polyphosphate in vitro. *Journal of Biomedical Materials Research Part B: Applied Biomaterials: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials* 89 (2), 430–438.
- Su, Y., *et al.*, 2019. Interfacial zinc phosphate is the key to controlling biocompatibility of metallic zinc implants. *Advanced Science* 6 (14),
- Subramani, K., *et al.*, 2016. In vitro evaluation of osteoblast responses to carbon nanotube-coated titanium surfaces. *Progress in Orthodontics* 17 (1), 23.

- Tang, Z., *et al.*, 2017. Potential biodegradable Zn-Cu binary alloys developed for cardiovascular implant applications. *Journal of the Mechanical Behavior of Biomedical Materials* 72, 182–191.
- Taylor, S.L., *et al.*, 2018. NiTi-Nb micro-trusses fabricated via extrusion-based 3D-printing of powders and transient-liquid-phase sintering. *Acta Biomaterialia* 76, 359–370.
- Thompson, G., Puleo, D., 1996. Ti-6Al-4V ion solution inhibition of osteogenic cell phenotype as a function of differentiation timecourse in vitro. *Biomaterials* 17 (20), 1949–1954.
- Thomsen, P., *et al.*, 1997. Structure of the interface between rabbit cortical bone and implants of gold, zirconium and titanium. *Journal of Materials Science: Materials in Medicine* 8 (11), 653–665.
- Toussaint, N.D., Kerr, P.G., 2007. Vascular calcification and arterial stiffness in chronic kidney disease: Implications and management. *Nephrology* 12 (5), 500–509.
- Tsuda, T., *et al.*, 1992. Inorganic arsenic: A dangerous enigma for mankind. *Applied Organometallic Chemistry* 6 (4), 309–322.
- Tsuda, T., *et al.*, 1995. Ingested arsenic and internal cancer: A historical cohort study followed for 33 years. *American Journal Of Epidemiology* 141 (3), 198–209.
- VanPutte, C., Regan, J., Russo, A., 2016. *Anatomia e Fisiologia de Seeley-10ª Edição*. McGraw Hill Brasil.
- Velmar, T., *et al.*, 2016. Biomaterials and host versus graft response: A short review. *Bosnian Journal of Basic Medical Sciences* 16 (2), 82.
- Verstraeten, S.V., Aimo, L., Oteiza, P.I., 2008. Aluminium and lead: Molecular mechanisms of brain toxicity. *Archives of Toxicology* 82 (11), 789–802.
- Viriyavejkul, P., *et al.*, 2007. Comparison of characteristics of patients with and without calcium pyrophosphate dihydrate crystal deposition disease who underwent total knee replacement surgery for osteoarthritis. *Osteoarthritis and Cartilage* 15 (2), 232–235.
- Waksman, R., *et al.*, 2006. Safety and efficacy of bioabsorbable magnesium alloy stents in porcine coronary arteries. *Catheterization and Cardiovascular Interventions* 68 (4), 607–617.
- Waksman, R., *et al.*, 2008. Short-term effects of biocorrosible iron stents in porcine coronary arteries. *Journal of Interventional Cardiology* 21 (1), 15–20.
- Wan, Y., *et al.*, 2016. Mechanical and biological properties of bioglass/magnesium composites prepared via microwave sintering route. *Materials & Design* 99, 521–527.
- Wang, K., *et al.*, 2008. The effect of polymeric chain-like structure on the degradation and cellular biocompatibility of calcium polyphosphate. *Materials Science and Engineering: C* 28 (8), 1572–1578.
- Wang, X., *et al.*, 2019. In vivo study of the efficacy, biosafety, and degradation of a zinc alloy osteosynthesis system. *Acta Biomaterialia* 92, 352–361.
- Weigand, E., Boesch-Saadatmandi, C., 2012. Interaction between marginal zinc and high fat supply on lipid metabolism and growth of weanling rats. *Lipids* 47 (3), 291–302.
- Williams, D., 1987. Tissue-biomaterial interactions. *Journal of Materials Science* 22 (10), 3421–3445.
- Williams, D., 2006. New interests in magnesium. *Medical Device Technology* 17 (3), 9–10.
- Witte, F., *et al.*, 2008. Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State and Materials Science* 12 (5–6), 63–72.
- Witte, F., 2010. The history of biodegradable magnesium implants: A review. *Acta Biomaterialia* 6 (5), 1680–1692.
- Witte, F., Eliezer, A., 2012. Biodegradable metals. In: Eliaz, N. (Ed.), *Degradation of Implant Materials*. Springer, pp. 93–109.
- Wong, C.-C., *et al.*, 2019. Biocompatibility and osteogenic capacity of Mg-Zn-Ca Bulk metallic glass for rabbit tendon-bone interference fixation. *International Journal of Molecular Sciences* 20 (9), 2191.
- Wong, P.-C., *et al.*, 2017. Degradation behavior and mechanical strength of Mg-Zn-Ca bulk metallic glass composites with Ti particles as biodegradable materials. *Journal of Alloys and Compounds* 699, 914–920.
- Wong, R., *et al.*, 2011. Effect of replacement of mandibular defects with a modular endoprosthesis on bone mineral density in a monkey model. *International Journal of Oral and Maxillofacial Surgery* 40 (6), 633–639.
- Woolf, A., *et al.*, 2002. A child with chronic manganese exposure from drinking water. *Environmental Health Perspectives* 110 (6), 613–616.
- Xin, Y., *et al.*, 2008. Influence of aggressive ions on the degradation behavior of biomedical magnesium alloy in physiological environment. *Acta Biomaterialia* 4, 6.
- Yamamoto, A., Honma, R., Sumita, M., 1998. Cytotoxicity evaluation of 43 metal salts using murine fibroblasts and osteoblastic cells. *Journal of Biomedical Materials Research: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and the Australian Society for Biomaterials* 39 (2), 331–340.
- Yan, Y., *et al.*, 2017. Improvement of the mechanical properties and corrosion resistance of biodegradable β -Ca₃(PO₄)₂/Mg-Zn composites prepared by powder metallurgy: The adding β -Ca₃(PO₄)₂, hot extrusion and aging treatment. *Materials Science and Engineering: C* 74, 582–596.
- Yang, L., Xi, G., 2016. Preparation and electrochemical performance of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials for lithium-ion batteries from spent mixed alkaline batteries. *Journal of Electronic Materials* 45 (1), 301–306.
- Yuen, C., Ip, W., 2010. Theoretical risk assessment of magnesium alloys as degradable biomedical implants. *Acta Biomaterialia* 6 (5), 1808–1812.
- Zhang, B., *et al.*, 2018b. Effects of YSZ and nano-ZrO₂ contents on the properties of Ti2448-ZrO₂ biomedical composites fabricated by SPS. *Ceramics International* 44 (11), 13293–13302.
- Zhang, E., Chen, H., Shen, F., 2010. Biocorrosion properties and blood and cell compatibility of pure iron as a biodegradable biomaterial. *Journal of Materials Science: Materials in Medicine* 21 (7), 2151–2163.
- Zhang, M., *et al.*, 2018a. Effect of a biomimetic titania mesoporous coating doped with Sr on the osteogenic activity. *Materials Science and Engineering: C* 91, 153–162.
- Zheng, H., *et al.*, 2017. Effects of MgO modified β -TCP nanoparticles on the microstructure and properties of β -TCP/Mg-Zn-Zr composites. *Bioactive Materials* 2 (1), 1–9.
- Zheng, Y., *et al.*, 2010. In vitro degradation and cytotoxicity of Mg/Ca composites produced by powder metallurgy. *Acta Biomaterialia* 6 (5), 1783–1791.
- Zheng, Y., Gu, X., Witte, F., 2014. Biodegradable metals. *Materials Science and Engineering: R: Reports* 77, 1–34.
- Zhong, X., Wong, W., Gupta, M., 2007. Enhancing strength and ductility of magnesium by integrating it with aluminum nanoparticles. *Acta Materialia* 55 (18), 6338–6344.
- Zhou, Y.-L., *et al.*, 2013. Microstructures, mechanical properties and in vitro corrosion behaviour of biodegradable Mg-Zr-Ca alloys. *Journal of Materials Science* 48 (4), 1632–1639.
- Zhu, D., *et al.*, 2017. Biological responses and mechanisms of human bone marrow mesenchymal stem cells to Zn and Mg biomaterials. *ACS Applied Materials & Interfaces* 9 (33), 27453–27461.

Joining of Metal Matrix Composites

VK Bupesh Raja, Sathyabama Institute of Science and Technology, Chennai, India
Manoj Gupta, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction to Metal Matrix Composites

Metal Matrix Composites, if designed and processed judiciously, can display the unique combination of properties of the matrix metal or alloy and the reinforcing materials. MMCs can, for example, display high thermal and mechanical response when compared to their monolithic metallic counterpart. In spite of many virtues, the applications of MMCs as structural material is limited due to the challenges in producing good quality weldments. The basic problem in welding the MMCs is the nature of the matrix reaction with the reinforcement at high temperature associated with the molten weld pool. This interaction of the matrix with reinforcement, if not controlled, leads to embrittlement of the matrix and decrease in the matrix/reinforcement interface strength. Hence, the fusion welding processes viz., Gas Tungsten Arc Welding (GTAW), Gas Metal Arc Welding (GMAW), Laser Beam Welding (LBW), etc., are difficult to use to join MMCs.

In this context soldering, brazing and solid state joining processes viz., friction welding, diffusion bonding, friction stir welding, etc., are ideal techniques for joining MMCs since in these techniques the high temperature and melting of the base material is avoided. When compared with solid state welding, soldering and brazing have critical applications, i.e., joining precisely intricate parts and joining large surfaces, respectively.

Classification of MMCs

Metal matrix composites can be classified based on the type of reinforcement used namely: particulate, whisker or short fiber, continuous multi filament and continuous mono filament and interconnected filaments (Campbell, 2011); the matrix material used, and primary and secondary processing techniques used.

Designation of Metal Matrix Composite

For metal matrix composites having metal or alloy matrix and reinforced with reinforcement in various percentages are designated as below:

Alloy (or) Metal/Particle/Percentage of reinforcement
Example: AA6061/TiO₂/20p

Where, p is used to represent particulates, w is used to represent whiskers and f is used to represent fiber. In this example, 6061 series aluminum alloy matrix is added with 20% of TiO₂ reinforcement particles to form the AMMC (Aluminum Metal Matrix Composite) (Ureña *et al.*, 1997).

Mechanical and Metallurgical Aspects of MMCs

MMCs normally exhibit improved strength than their metallic counterparts. The extent of increase in strength, however, is not very significant when compared to their increased elastic modulus (Mallick, 2016).

The rule of mixture expression for computing elastic modulus of MMCs can be written as:

$$E_c = V_p E_p + V_m E_m \quad (1)$$

Where, E_c is the moduli of the composite, E_p is the moduli of the particulates, E_m is the moduli of the matrix, V_p is the volume fraction of particulates, and V_m is the volume fraction of the matrix.

Eq. (1) is reasonably accurate for the continuous reinforcement, while Eq. (2) is appropriate for the discontinuous reinforced MMCs (Halpin, 1984).

$$E_c = E_m \left(1 + 2sqV_p \right) / \left(1 - qV_p \right) \quad (2)$$

Where, s is the aspect ratio of the particulate and

$$q = (E_p/E_m - 1) / (E_p/E_m - 2s) \quad (3)$$

The Young's modulus is dependent upon the volume fraction of reinforcement and it is not much affected by the distribution of the particles. The increase in strength of the MMCs containing micron and sub-micron size ceramic particulates is associated with decrease in percentage of elongation. The ductility of the MMCs for these length scales is strongly influenced by the distribution of the

particles. The homogeneity of the microstructure of the MMCs is strongly influenced by the type of primary and secondary processing of the material. The recrystallization of grains in MMCs is affected during heat treatment, by the volume fraction of the particles and their size. The reactivity between the matrix and reinforcing particles influence the choice of processing to be selected.

Applications of Metal Matrix Composites

In almost the past four decades MMCs are mostly made using aluminum and its alloys as matrix material, as they replaced heavier cast iron and steels in many applications. Magnesium based MMCs are emerging as an alternate light weight replacement for aluminum based MMCs. The continuous reinforcements like boron fibers and graphite fibers are restricted to aerospace applications, due to their high cost, lack of secondary fabrication capabilities and non-availability in various shapes (Mallick, 2016). The cheap reinforcements namely short staple mullite fiber and Al_2O_3 are used to enhance wear resistance through selective reinforcement of engine parts like the ring land area of diesel engine pistons (Dinwoodie *et al.*, 1985; Stacey, 1988; Donomoto *et al.*, 1983). Discontinuously reinforced MMCs generally use particulates as reinforcement. The ceramic particles like Al_2O_3 and SiC are used in MMCs due to their low cost and ease of fabrication using existing conventional fabrication machineries. By virtue of their low aspect ratio, they impart isotropic properties similar to their matrix metal/alloy and hence are used in commercial fabrication of brake rotors, bicycle frames, wear resistant studs, cylinder liners, thrust plates, wrought and cast components, and thermal spray coatings (Mallick, 2016). The graphite/aluminum discontinuous reinforced aluminum composites (DRAs) are used in tribological application as they display superior wear resistance, anti-friction and anti-seizure behavior (Campbell, 2011). Generally, the volume fraction of reinforcement is kept less than 25 vol%. MMCs with more than 25 vol% reinforcement are used in applications like thermal management systems, electronic packaging and high temperature applications, which require high thermal conductivity and low coefficient of expansion (Lloyd, 1994; Mallick, 2016).

Joining of MMCs Through Fusion Techniques

Challenges in Fusion Welding of MMCs

The welding of MMCs through fusion welding processes namely Gas Tungsten Arc Welding (GTAW), Gas Metal Arc Welding (GMAW), Laser Beam Welding (LBW), Electron Beam Welding (EBW), etc., pose a challenge due to the following issues (Ellis, 2007):

- (1) High Viscosity of Molten MMC: Due to the presence of reinforcing particles or fibers in the matrix the viscosity of the molten weld pool of the MMCs is higher than that of the matrix alloy. This makes it impossible, to manipulate the weld pool and to ensure the homogenous distribution of the particles. As the temperature of the weld pool is increased the viscosity can be reduced but metallurgical reactions between the particles and the matrix increases. The viscosity is also affected by the amount of reinforcement and their size and shape. The use of autogenous gas tungsten arc welding, i.e., without filler wire, is effective but it behaves like brazing, yielding minimal dilution in the fusion zone and the heat affected zone of the parent MMC material.
- (2) Reinforcement Particle/matrix Reaction: The differences in melting point of reinforcement particles/fibers and the matrix, high thermal expansion co-efficient differences and difference in thermal cycles causes thermal stresses in welding and triggers reaction between the reinforcement particles and the matrix (Bhattacharyya *et al.*, 1992). At high temperatures, the reinforcing particles react or dissolve in the matrix and form detrimental compounds upon cooling. Mostly these products of particle/matrix reaction have needle shaped morphology which act as stress concentration points during loading and make MMCs prone to corrosion (Dahotre *et al.*, 1991). These reactions can be controlled easily by using optimal process parameters and minimal weld heat in GTAW and GMAW where inert gas shielding is provided. This reaction can be controlled by optimizing the process parameters in power beam welding processes like EBW and LBW, wherein LBW is much sensitive, but the former is almost immune as the process is carried out in vacuum. The selection of suitable electrode/filler wire compatible with the chemical composition of the matrix slows down the reaction between particles and the matrix. The reaction between particles and matrix is not been reported in solid state welding, in particular, the resistance spot welding.
- (3) Segregation of Reinforcing Particles: The segregation of reinforcing particles occurs in micro and macro scale during welding. In the GTAW and GMAW, the particles are pushed by the solidification front, resulting in a micro-scale segregation of reinforcing particles. This behavior is not observed in the LBW and EBW which have rapid thermal cycle (Dahotre *et al.*, 1991). In the case of resistance spot welding, macro segregation is observed where a large variation in the distribution of the particles exists across the weld nugget. The mechanism causing this heterogenous distribution of particles in resistance spot welding is not clear. This can be controlled by selection of proper process parameters (Gittos and Threadgill, 1991).
- (4) Release of Occluded Gases: The occluded gases particularly hydrogen poses a problem in the MMCs fabricated through powder metallurgy process. During fusion welding, the melting of MMCs causes the release of occluded gases from the solid solution which causes embrittlement of the heat affected zone and porosity in the weld fusion zone and heat affected zone. The occluded gases can be removed by vacuum degassing of the metal powders before the fabrication of the MMC (Ellis, 1996).

The application of fusion welding techniques to weld MMCs has its own challenges as the high temperature involved in fusion welding sets ideal conditions for chemical reaction between matrix and the reinforcement particles leading to the formation of intermetallics, oxides and change in grain size. These conditions are detrimental for the strength of the MMCs (Ureña *et al.*, 1997; Holcomb, 1991). The homogeneous distribution of the reinforcement particles is interrupted in the MMC molten pool and likely to be absent in the joint. The use of a MMC filler rod or the post weld treatment (spheroidization treatment) have not much effect in improving the properties or minimizing the heterogeneous distribution of reinforcement or its absence in the joint or their agglomeration (Clyne and Withers, 1993). Hence the solution to these limitations is to apply heterogeneous joining techniques like brazing where low fusion temperature filler is used to join the metal matrix composite. Mostly it is applied in joining aluminum based MMCs (Sugiyama, 1989).

Low Heat Intensity Fusion Welding: Gas Tungsten Arc Welding and Gas Metal Arc Welding

The low intensity heat input fusion welding processes that are commonly used to join MMCs are Gas Tungsten Arc Welding and Gas Metal Arc Welding. As in metals and alloys, the alternating current is used while welding aluminum (2xxx and 6xxx) based MMCs since it breaks down the oxide film on the surface of the metal. The Discontinuously Reinforced Aluminum Matrix Composite (DR-AMC) having SiC as reinforcing particles are welded with high silicon filler wires such as ER 4047. Similarly in the case of MMCs with Al₂O₃ reinforced particles, high magnesium filler wire are used (Ellis, 1996). The presence of reinforcing particles in the MMC weld pool hinders their homogenous mixing and leads to agglomeration, segregation and dewetting. The addition of fibers in 6061 Al-B MMC and welding autogenously caused dissolution and filament (fiber) fragmentation (Laurent *et al.*, 1987). This could be solved by using silicon rich filler which protects the outermost layers of Boron filaments and improve their wettability. AA6061 aluminum alloy having 15 vol% SiC of 10 µm size when welded using GTAW yielded good quality welds (Xi-he *et al.*, 2009). The addition of 50 vol% helium with argon of 99.99% purity and the use of Al-Si filler wire resulted in a stable arc with no spatter, higher energy density, deeper weld penetration, and the undesirable interface reactions were prevented thus simultaneously improving the mechanical properties of the welded joints.

During welding of aluminum based MMCs containing SiC reinforcing particles, the liquid-phase processing leads to conditions favorable for interfacial reactions to take place between aluminum and SiC to form needle like phases namely Al₄C₃, Al₄Si₂C₅, Al₄SiC₄, and free silicon (Ureña *et al.*, 2000; Shin *et al.*, 1997; Viala *et al.*, 1993; Ahearn *et al.*, 1982). The formation of Al₄C₃ occurs at the expense of SiC particles added for reinforcing the matrix.



The needle-like Al₄C₃ is prone to hydrolysis leading to corrosion of the MMCs (Park and Lucas, 1997). The free silicon creates Al-Si eutectic aggregates on the particle-matrix interface and at the grain boundaries of the matrix, causing loss of ductility. The welding at lower temperatures could prevent/minimize the interfacial reactions and thereby producing good quality welds.

The gas metal arc welding of AA7020 (Al-Zn-Mg) and AA7005 reinforced with 10 vol% of Al₂O₃ particles was done using ER44043 (Al-Si) and ER5356 (Al-Mg) fillers. In the welds carried out with ER44043 filler, the formation of hypoeutectic interdendritic structures having Al-Si precipitates in the interdendritic locations was observed (Salazar and Barrena, 2003). The post weld T6 artificial aging converted the microstructure to one with spheroidized morphology with recrystallized aluminum, which increased the toughness. Further, the post weld heat treatment caused precipitation of the hardening Mg₂Si phases and improved the hardness of the welded joint (Gómez de Salazar and Barrena, 2002).

The joints welded with ER5356 filler exhibited dendritic structure with the formation of primary aluminum and secondary phase (Mg₂Si) in the inter-dendritic location. This was caused due to the excess magnesium in the filler wire. The presence of Al₂O₃ particles decreased the thermal diffusion and thus maintained the MMC at high temperature for long period. This annealing condition caused dissolution of hardening phases and loss of mechanical properties which was reversed upon post weld T6 aging heat treatment.

The nitrogen gas plasma arc welding of SiCp/Al MMC was used to carryout in situ alloying to improve the mechanical properties of welded joints. The use of titanium as a filler material for the in situ alloying eliminated the formation of the detrimental Al₄C₃ phase in the MMC. The welding heat caused the recrystallization of the aluminum matrix. Since the free energy involved in the formation of TiC is much lower than that of Al₄C₃, the TiC formation occurred readily thus suppressing the formation of Al₄C₃. Similarly, the reaction between aluminum and nitrogen from the ionized gas takes place yielding AlN₂ and TiN, and suppressed the formation of Al₄C₃.

When compared with TiC and TiN, TiN has lower free energy and hence TiN is easily formed. The formation of new hard phases TiC, TiN, Al₃Ti, and Ti₅Si₃, compensated the loss of SiC due to its dissolution in the weld pool and improved the mechanical properties.

High Heat Intensity Fusion Welding: Laser Beam Welding and Electron Beam Welding

The high heat intensity welding processes are characterized by the low heat input associated with the fast thermal cycle, such as in the Laser Beam Welding and Electron Beam Welding processes (Ellis, 1996). The laser beam coupling, i.e., the interaction of the beam with the material is around four times higher for MMCs when compared with the monolithic alloys. Hence the laser beam

welding is more effective on MMCs. Majority of laser beam welding are carried out on Aluminum/SiC MMCs using Continuous Wave (CW) CO₂ laser and Pulsed Nd:YAG laser.

The A356–20% SiC MMC when welded with CO₂ laser in key-hole mode yielded welded joints showing formation of Al₄C₃ through dissolution of SiC and Si enrichment of the aluminum matrix and thus resulting in loss of toughness and causing brittleness of the joint (Bassani *et al.*, 2007). Even though the amount of Al₄C₃ can be minimized by choosing proper welding parameters, but the formation of Al₄C₃ phase cannot be totally avoided. The conduction mode with diode laser caused much lower increase in temperature and hence the SiC dissolution was limited and their uniform distribution produced joints with good mechanical properties. The only drawback in the diode laser is lack of penetration, which can be compensated by using high power diode lasers.

The in-situ alloying with titanium while joining SiCp/6061 Al MMC using CO₂ laser was found to be effective in completely eliminating the formation of the needle-like detrimental aluminum carbides (Wang *et al.*, 2000).

The laser and electron beam welding of fine grained Al6061/SiC MMC with 1%, 5%, and 20% SiC, produced welded joints exhibiting High Strain Rate Superplasticity (HSRS). The presence of SiC particles improved the beam coupling of the laser and hence the welding was of better quality in LBW, than the EBW process. The fusion zone of LBW welded Al6061/SiC MMC exhibited occasionally shallow cavities on the weld cap whereas in the case of EBW a V shaped notch was observed (Huang *et al.*, 2001).

The increased SiC content increased the laser beam absorption efficiency but it caused formation of Al₄C₃ and embrittlement of the welded joints. Hence the fine grain structure was lost and efficiency of HSRS weldments was lost. Thus the LBW and EBW for HSRS is not practically feasible.

The CO₂ laser beam welding of TiB₂ particles reinforced aluminum matrix composite exhibited agglomeration in the middle of the weld bead. The laser energy absorption efficiency of TiB₂ particles is greater than the surrounding aluminum matrix and hence they melt and merge together to form clusters of TiB₂. The partially molten TiB₂ particles react with the molten aluminum matrix resulting in the interfacial reaction. AlB₁₂ and Al₃Ti were formed as a result of reaction and were reported to be harmful for the welded joints. Meng *et al.* (2013) also observed that the aluminum near to the key hole of the laser gets vaporized and the thermal stress was caused in the TiB₂ which are inside and around the key hole, as they undergo uneven expansion due to sharp temperature gradients.

The pulsed Nd-YAG laser welding of SiC reinforced Al–Cu–Mg MMC proved that good quality welds can be produced by controlling the laser parameters such as laser intensity and a long pulse-on time. This ensured minimal formation of Al₄C₃ and welding defects like thermal cracking and porosity (Yue *et al.*, 1997).

The YAG solid pulsed laser welding of silicon carbide whisker (SiCw) reinforced 6061 Al MMC yields weld strength of around 70% of the parent MMC. This was realized by improving the weld quality by decreasing the heat input of the weld pool and increasing the silicon carbide content in the weld pool (Niu *et al.*, 2006).

The addition of a 0.05 mm thick foil of 99.99 wt% pure Zr in the weld zone improved the tensile strength of the fiber laser welded 10 vol% SiC particles (SiCp) reinforced MMC. The porosity in the weld zone was eliminated by the alloying with Zr. The addition of Zr in the weld zone improved the wettability of the SiCp and reduced the viscosity of weld pool and hence permitted the escape of the bubbles from the weld pool. Zirconium reacted with SiCp and formed ZrC phase which was dispersed throughout the weld zone and improved the properties of the welded joints (Long *et al.*, 2020).

The dissimilar metal joints of 6061 aluminum alloy and MMC reinforced with TiB₂ particles using Nd-YAG pulsed laser was influenced by the laser power followed by laser frequency and welding speed. The phases such as Al₂Ti, Fe₂Si, and Al_{0.5}Fe₃Si_{0.5} and free aluminum were formed in the weld zone with the decomposition of TiB₂ particles upon reaction with Al. The unreacted TiB₂ particles solidified and the excess TiB₂ particles segregated at the grain boundaries by the molten Al. The TiB₂ particles were well wetted by the molten aluminum matrix which enhanced the corrosion resistance of the weld zone (Dai *et al.*, 2019).

The YAG laser welding of AA1100–16vol% B₄C MMC resulted in the decomposition of B₄C and the formation of needle-like AlB₂ and Al₃BC phases. Alloying with a 150 µm thick Ti foil decreased the needle like phase formation and improved the tensile strength. Whereas, the use of filler wire along with Ti alloying, led to its segregation and loss of tensile strength (Guo *et al.*, 2012).

Joining MMC Through Solid State Techniques

Friction Welding Processes

Friction welding is one of the popular technique to join MMCs. Friction welding is of various types such as rotary, inertia and linear. The friction between the moving components produces heat which causes the plastic extrusion-forging of the mating parts. The general behavior of friction welding is that, the reinforcing particles either break or crushed at the interface of the components in movement or at the tool-component interface. The heat affected zone tends to be softened leading to reduction of hardness (Ellis, 1996).

Friction Stir Welding (FSW) involves a rotating tool with a pin plunged into the joint interface resulting in frictional heat leading to the plasticizing of the metal and its extrusion and recirculation causing the formation of the welded joint (Vijay and Murugan, 2010). The rotating pin and shoulder irons the extruded and recirculated plasticized metal and forms a stir zone where the joint is formed. There is exhaustive literature on the influence of tool profile and the FSW process parameters on the

microstructure and the mechanical properties of various AMCs (Chen *et al.*, 2009; Fernandez and Murr, 2004; Wert John, 2003; Marzoli Gambaro *et al.*, 2006).

The profile of the pin and shoulder ensures sufficient frictional heat generation and formation of the weld nugget or joint. The proper selection of the FSW process parameters yields defects free joints, which otherwise end up with worm holes, tunnel defects etc.

The friction stir welding of AMC with 10 wt% of TiB_2 with a straight square pin profile yielded a narrow stir zone having a fine grained microstructure with homogeneous distribution of the TiB_2 particles, much better than the parent AMC and exhibited good mechanical properties (Vijay and Murugan, 2010).

The friction stir welded 20 wt% $\text{B}_4\text{Cp}/6061 \text{ Al-T6}$ AMC processed with a threaded cermet tool caused fragmentation and blunting of the B_4C particles which were homogeneously distributed in the nugget zone. This was due to severe particle/pin interaction and resulted in dissolution of the fine precipitates in the nugget zone and the loss of tensile strength of the friction stir welded joints. The use of optimized FSW parameters improved the weld quality and the mechanical properties. Further improvement of the properties was realized through artificial aging which resulted in re-precipitation and improvement of the mechanical properties (Li *et al.*, 2019).

The friction stir welding was also applied to join bulk metals, alloys, MMCs and dissimilar materials. The same FSW in a modified form called as Friction Stir Processing (FSP) was used to do surface engineering of the materials. In this context, the FSP was carried out to produce Surface Composites (SC), i.e., MMC was confined to the surface of the metal based material.

AA7050-T7451 (Al-Zn-Mg-Cu) alloy processed by FSP was butt welded with FSW. They on further friction stir welding yielded uniform distribution of the hybrid reinforcement particles of TiB_2 , Al_2O_3 , Mg, and Zn and also exhibited uniform hardness. Incidents of minute tunneling defects and Incomplete Root Penetration (IRP) were observed, which can be prevented with selection of suitable FSW parameters (Haider *et al.*, 2019).

The rotary friction welding of A6061 with 10 vol% Al_2O_3 with the similar AMC and with the base A6061 alloy yielded good results indicating that friction welding is ideal for welding MMCs. The increase in friction pressure decreased the thickness of the intermetallic film and encouraged disruption and removal of the oxide films from the joint interface through the formation of flash thus directly increasing the tensile strength of the welded MMCs (Maldonado, 1997).

The dissimilar and similar linear friction welding (LFW) of 2024 Al alloy and 2124 Al/SiCp MMC resulted in good weld joint efficiency with a decrease in elongation. This decrease in elongation was attributed to orientation of the plastic flow of metal in the Thermo-Mechanical Affected Zone (TMAZ) which undergoes severe plastic deformation. The weld zone exhibited ultra-fine microstructure with uniform distribution of the reinforcement particles (Ceschini *et al.*, 2010).

Solid State Diffusion Bonding of MMCs

The hard protruding reinforcing particles existing in the planar interface penetrates into the soft matrix leading to ideal bonding. Situation of a non-planar interface could occur when the protruding reinforcing particles between the planar bond line at the interface of the faying surface interlock and thus contributing to higher bond strength (Shirzadi *et al.*, 2001). The increase in bond strength was attributed to the reinforcing particles rupturing the oxide layer in their vicinity (Partridge and Dunford, 1991; Shirzadi, 1998).

Joining MMC Through Bonding

Diffusion bonding of MMC can be carried out through conventional transient liquid phase (TLP) bonding, solid state diffusion bonding and the temperature-gradient transient liquid-phase diffusion bonding (Shirzadi *et al.*, 2001).

In diffusion bonded MMC-MMC joints the bond line is studied keeping in view the interfaces, namely; matrix-matrix interface, matrix-particle interface, and particle-particle interface. The volume fraction of the reinforcing particles in the faying surface and their distribution, decides the area fraction of the bond line interface (Partridge and Dunford, 1991).

Transient Liquid-Phase (TLP) Diffusion Bonding of MMCs

In transient liquid-phase diffusion bonding, an interlayer is introduced between the faying surfaces. The interlayer may have a lower melting point or form a liquid eutectic phase which lowers the melting point of the matrix in its vicinity. This causes diffusion between the faying surfaces and the adjoining liquid interface and solidifies isothermally at the bonding temperature at which the material is soaked. During this process the oxides, impurities and reinforcing particles get agglomerated and get pushed forward towards the planar bonding line by the advancing solid-liquid boundaries (Maddrell, 1989).

Temperature-Gradient TLP Diffusion Bonding of MMCs

In temperature-gradient TLP diffusion bonding a temperature gradient is maintained during TLP leading to the formation of non-planar bond line having higher metal to metal interface (Assadi *et al.*, 2001). These interfaces are wavy having sinusoidal to

dendritic morphology, with unbounded areas and voids in between them. By controlling the temperature gradient, thickness of interlayer and size of reinforcing particles, strengths equivalent to the parent MMC material can be achieved with high metal-to-metal contact (Zhai and North, 1997). Hence comparing solid-state bonding and TLP; this technique produces reliable high strength joints.

Adhesive Bonding of MMCs

The SiCp reinforced aluminum MMC sheets can be bonded at room temperature using adhesive bonding method. The adhesive bonding does not involve any thermal cycle which causes undesirable chemical reactions producing detrimental intermetallic compounds. Even though the adhesives such as toughened acrylic, epoxy resin, nitrile phenolic etc. produce good bonding, but its effectiveness depends on the surface pretreatments. The surface pretreatment such as chromic acid anodizing and silane pretreatments are established to produce good bonding of the substrate with the SiC particles which hook themselves to the pretreated surface. But the disadvantage of these pretreatments is the poor durability of the bonds and they are detrimental in nature. Hence the etching or abrasion of the bonding surfaces is sufficient to yield good bonding for adhesive bonded MMCs (Ellis, 1996, 2007).

In the case of Glass Laminate Aluminum Reinforced Epoxy (GLARE) fiber metal laminates, thin layers of metal sheets are stacked in between unidirectional fiber layers which are bonded to the metal layers using adhesive. The pretreatment of the metal fraying surface involves chemical cleaning through phosphoric acid anodizing or chromic acid anodizing process. The chemically cleaned surfaces are made durable and corrosion resistant by treating with corrosion inhibiting primer. The bonding between the adhesive and the fibers are very strong and the failure occurs through cohesive adhesive failure. The GLARE possesses good resistance to fatigue crack propagation and good strength at a lighter weight and cheaper cost when compared with the bulk metal. In order to manufacture the GLARE at cheaper cost and produce compatible forms and shapes, self-forming technique (SFT) is used (Vlot and Gunnick, 2001).

Joining Using Brazing and Soldering

Brazing of MMCs and Using MMCs for Joining

The brazability of MMCs is dependent on the wettability of the filler material by the MMC matrix, which is influenced by the following:

- (1) The liquidus temperature of the filler metal. The filler metal having a liquidus temperature lower than melting point of the constituents of the matrix. The filler with eutectic composition is regarded as having the best wettability. The wettability of the filler droplet is governed by the spread ratio (SR) and contact angle (θ). The spread ratio is the ratio between total area wetted by the molten metal, to the original area of the filler metal (Humpston and Jacobson, 1993). The contact angle is the angle made by filler drop with the surface of the matrix. Generally an angle less than 90° is advised and contact angle lower than 20° is preferred for brazing (Nicholas, 1989).
- (2) The viscosity of molten filler. The viscosity of the molten filler decides the required wettability or the flow out of the filler from the joint leading to voids and unwanted wetting on the parts other than the joint. At high temperatures, the viscosity of the molten filler is affected by the percentage of ceramic particles. The presence of reinforcement causes formation of solid phases in the molten filler drop and reduces the spreading and diffusion of the molten filler on the matrix metal (Klomp, 1989).
- (3) The dissolution of the elements from the matrix into the molten filler metal reduce its wettability due to the formation of primary solid phase in the presence of ceramic reinforcement particles.
- (4) Increase in brazing cycle causes changes in the grain size, which affects the properties of the MMC.

Several brazing techniques have evolved to braze MMCs and a few of them are discussed below:

- (1) Vibration assisted brazing: The SiCp/A356 MMC brazed using an experimental setup that could bond the joint at 375°C with the assistance of mechanical vibration showed that the oxide layer was disrupted and removed due to vibrations during brazing with Zn–Al eutectic filler alloy. Even though the bonding was realized, it had porosity. The porosity was removed upon continuously heating the joint upto 520°C leading to an enhancement in strength beyond that of the base MMC material (Yan *et al.*, 2008).
- (2) Electromagnetic field aided brazing: The behavior of SiC particles in MMCs during joining is critical and hence it has to be kept under control. In this connection a new method of brazing called as electromagnetic field aided brazing (EMFAB) was developed. In the EMFAB brazing of SiCp/A356 MMC using Zn–Al filler alloy, the magnetic intensity of 0.5T aided in the homogeneous distribution of SiC particles in the brazing seam with room for the inherent nature of segregation at the joint interface (Yu *et al.*, 2010).
- (3) Vacuum brazing: Brazing being a heterogeneous joining process is preferable in joining MMC/MMC and MMC/alloys. The joining of SiCp/6063Al MMC with Fe–Ni alloy using vacuum brazing with a filler metal Ag47–Cu18–In17–Sn17–Ti–1 was

carried out at a temperature of 580°C. The soaking of the filler and the joint material at 580°C for 30 min under vacuum created ideal conditions for the diffusion of Ag, Sn and In into the SiCp/6063 Al MMC thereby led to the formation of a good joint. But this process affected the strength of the joint when the brazing temperature exceeded 580°C (Gao *et al.*, 2016). Vacuum brazing of a titanium based alloy Ti-48Al-2Cr-2Nb and TiC/Ti metal matrix composite using Ag-28Cu filler alloy at high temperature of 850°C produced good joints with microstructure showing Ti-48Al-2Cr-2Nb/TiAl + AlCuTi/AlCu₂Ti/Ag/AlCu₂Ti/Ti₂Cu/Ti as a new MMC. With the increase of temperature the thickness of the brazing seam increased and there was a decrease in the Ag (solid solution) volume fraction and the AlCu₂Ti reaction layer disappeared followed by the formation of new phases namely Ti₃Al and Ti (Cu, Al) in the joint region, which improved the properties of the joint. However, the joints became brittle with increase in temperature to 1000°C wherein the Ti₃Al phase coarsening occurred and excess of Ti and Al diffused into the joint. Hence the increase in brazing temperature in the above system was shown to induce undesirable brittleness and loss of properties (Dongdong *et al.*, 2019).

- (4) Ultrasonic assisted brazing using MMC: In order to reduce the interfacial cracking of joints in sapphire blocks an interlayer having a sandwich structure comprising of MMC Zn-Al/(SiCp/A356)/Zn-Al was fabricated and placed below the Zn-Al filler alloy coated sapphire blocks. The whole setup was brazed under the influence of ultrasound. It was observed that the SiCp/A356 MMC was dissolved by the Zn-Al filler alloy to yield a new MMC of SiCp/Zn-Al-Si comprising of Zn-Al-Si alloy having around 40 vol% of SiC particles (Wei *et al.*, 2018).
- (5) Microwave assisted brazing using MMCs: Copper was joined by microwave irradiation using an interlayer comprising of copper powder dispersed in epoxy resin to hold the faying surfaces together and to prevent squeezing off of the inter layer. Charcoal was used as a susceptor to initiate initial heating of copper powder and due to its ability to couple with the microwaves. The joint obtained was crack free and had minimal porosity. The addition of 7% of carbon increased the hardness and aided in forming a good bond between the sandwich layer and the copper interfaces (Srinath *et al.*, 2011).
- (6) Oxyacetylene brazing for preparing MMC filler: In yet another unique study, a MMC filler material was fabricated from a WC/W₂C, Cu and Mn powder by infiltration of a nickel based bronze (74.4 wt% Cu, 15.8 wt% Sn, 3.8 wt% Mn, and 5.5 wt% Ni). The MMC filler was fabricated using oxyacetylene brazing process with an Ag alloy brazing filler metal (49 wt%Ag, 23 wt% Zn, 16 wt%Cu, 7.5 wt%Mn, 4.5 wt%Ni). This MMC was brazed to WC-Co substrate of a Polycrystalline Diamond Compact (PDC) insert. The formation of an inter diffusion zone in the brazing showed phases like AgMn₁₉, Cu-Zn, and Mn-Zn which enhanced the bonding between the WC-Co cermet and the MMC (Bouzegzi *et al.*, 2018).

Solderability of MMCs

Solderability of MMCs was investigated by many researchers. Effect of plating on the faying surface was investigated by Lu *et al.* (2012). The nickel plating of Al356-SiC composite faying surface containing 55 vol% SiC particles showed that the nickel did not react with the Al356-SiC composite substrate during electroplating and it improved the wettability of the Zn-Cd-Ag-Cu solder alloy (Lu *et al.*, 2012). The electroplating process caused formation of gas pores of around 1 µm due to probable diffusion and accumulation of hydrogen. These pores aided in the mutual diffusion of the elements in the solder alloy, Ni plating layer and the Al356-SiC composite base material thus improving the wettability and strength of the Al 356-SiC MMC and Fe-Ni-Co alloy (commercially known as Kovar) joint. The Ni electroplating of the base MMC material with 55 vol% SiC particles improved the wettability of solder which otherwise would hinder it (Ernst Mikols and Burkhard Haas, 2003; Niu *et al.*, 2003; Wang *et al.*, 2009; Niu *et al.*, 2001; Enis, 1996).

The ultrasonic assisted soldering of Al-Cu-Mg (2024 Al) AMC eliminated the oxide layer and encouraged the bonding of the Zn-Al filler and AMC having 30 vol% of Al₂O₃ particles. The soldering strength increased with increase in time of exposure to ultrasonic vibrations (Xu *et al.*, 2012).

The presence of reinforcement in AMCs makes it challenging to solder. The high temperature soldering of AA2014 series aluminum based SiC reinforced composite using Zn-Al filler alloy was carried out in the temperature range of 400–450°C. The AMC was reinforced with discrete SiC particles of 6, 13, and 20 vol%. It was observed that the aluminum with more than 10 vol% of reinforcement tend to exhibit poor wettability. The presence of alloying elements like copper and magnesium led to intergranular penetration of the filler elements by their diffusion through the grain boundaries of the base matrix with partial melting of the matrix material and thus promoting the diffusion of zinc into the matrix. In cases where low melting point solders were used, it was observed that defects like erosion and lack of penetration occurs along with reduced strength (Ureña *et al.*, 2001).

Electronic Solder Composites

The use of Lead based solder composites is challenging. Further, the environmental concern about the use of lead (Pb) in the solder is also a major concern in soldering MMC. On the contrary, lead free solder composites possess enhanced bonding and mechanical strength compared with the conventional solder alloys. The addition of nano particles, carbon nano tubes, metal meshes, etc. have been explored to produce lead free composite solder materials.

The soldering of aluminum matrix composite fabricated through Equal Channel Angular Extrusion (ECAE) with SiC, Al₂O₃ particles reinforced upto 35 vol% using tin based solders, yielded good quality joints. This was attributed to the simultaneous

application of ultrasonic vibrations and heat treatment using a tube furnace. The ultrasonic vibrations ensured homogenous distribution of the particles in the solder and there were no new phases formed since the process was carried out between 250 and 280°C with the solders melting point being around 227°C. The main strengthening mechanism was due to the ability of the particles to arrest the movement of dislocations. Further the ultrasonic process aided in increasing the wettability of the solder (Weis *et al.*, 2008).

The Sn-Bi solder reinforced with SAC-BN particles made through mechanical mixing and soldered through reflowed solder method exhibited an unique behavior of change of grain size, till the addition of 0–8 wt% of SAC-BN particles. The Sn-rich phase was increased and the increase in grain size of β -Sn matrix was observed, leading to the increase in hardness and brittleness and reduction in mechanical properties. However, the doping of SAC-BN particles above 8 wt% led to refinement of grains and improvement in the mechanical properties (Liu *et al.*, 2016).

The lead free solder Sn–0.7Cu–0.05Ni with the addition of TiO₂ particles through microwave assisted sintering powder metallurgy method with TiO₂ in 0, 0.25, 0.5, 0.75, and 1.0 wt% yielded a composite solder. The microwave assisted sintering proved to be an ideal technique to ensure the uniform distribution of the TiO₂ particles in the lead free composite solder. The presence of TiO₂ caused the reduction in thickness of intermetallic compound layer and thus leading to improved ductility, hardness and shear strength of the soldered joint (Ramli *et al.*, 2016).

Lis *et al.* (2018) investigated the use of stiffening copper and nickel thin metallic meshes within SAC305 solder joints. The results showed formation of faceted Ni₃Sn₄ intermetallic at the surface of the copper mesh – SAC 305 (CMS) solder interface and nickel mesh and SAC 305 solder (NMS) interface. It caused a fracture pattern existing partially within the solder and partly in the solder-mesh interface. This phenomenon of mesh reinforcement increased stiffness by 5% in the case of NMS and 11% in CMS and locally increased fracture resistance.

Joining of Sandwich Composite – Explosive Welding

Sandwich composite materials are made of multiple layers of materials which comprises of laminates of metal or alloy with reinforcing fibers. These laminates are bonded together by means of adhesive bonding or cladded using solid state welding process like Explosive Welding (EW). The fabrication of aluminum sandwich composite reinforced with steel wire mesh was carried out through explosive welding. The steel wire mesh placed between two aluminum plates gets bonded with negligible heat transfer from one plate to another due to rapid release of energy from the explosion. The hardness of the joining interface was increased due to the work hardening effect associated with severe plastic deformation caused by the cold pressure applied by the explosion in explosive welding process. At the same time, the hardness of the matrix away from the joint interface exhibited a reduction in the hardness (Gülenç *et al.*, 2015).

The explosive welding of LY12 Aluminum plate/reinforcing steel fiber/304 L stainless steel plate showed that the ballistic resistance of the composite increased with the increase in density of reinforcing steel fiber (Zhou *et al.*, 2014).

The cold pressure welding of a sandwich composite comprising of stacks of alternate layers of stainless steel wire meshes and aluminum foils was fabricated through explosive welding method. The bonding is between the stainless steel fibers and the aluminum foil was attributed to extrusion of aluminum foil between the fibers of the reinforcing mesh, rather than through explosive welding (Bhalla and Williams, 1977).

The results indicate that explosive welding is an alternative and effective method of joining except for the risks that are inherently associated with this kind of joining.

Non Destructive Testing (NDT) of MMC Weldments

The agglomeration of coarse reinforcing particles which are not wetted leads to degradation of strength and ductility of the MMCs (Mallick, 2016). Further, the presence of porosity and other metallurgical defects leads to unreliability of the MMC components. Hence, there is a need for non destructive evaluation of MMCs to ensure reliability. The presence of defects and quality of MMC joints are assessed by NDT techniques both quantitatively and qualitatively. The quantitative evaluation involves the assessing of defects caused by the presence of reinforcement in the matrix. The quantitative evaluation using ultrasonic testing technique with suitable contraption of using aluminum layer between the ultrasonic transducer leads to determination of the presence of reinforcing particles in spite of the signal scattering and the attenuation effects. Pulse echo ultrasound immersion test are affected by the interface zone but could detect the presence of defects. X ray radiography or a Scanning Laser Acoustic Microscope (SLAM) yields good sensitivity to the presence of defects besides the presence of reinforcing particles. The acoustic microscopy is capable of detecting micro cracks and micro porosity in the MMC. However, the x-ray radiography is not suitable for in-situ evaluation. The application of micro focus x-ray radiography aids to analyze the components as a whole whereas the misorientations of fibers and the presence of macro pores can be determined. The eddy current gets distorted due to the presence of surface irregularities which mask the presence of subsurface defects (Ellis, 1996).

The qualitative analysis of MMC joints helps to investigate the position of the reinforcement, their orientation, volume fraction and distribution in the MMC. The qualitative analysis are carried out using optical microscope, scanning electron microscope,

tunneling electron microscope, etc. The combination of qualitative and quantitative techniques aid in determining the presence and the degree of defects in the MMC joints.

Concluding Remarks

The study of MMC is being carried out aggressively for almost past four decades. However, its wide application in structural components is not widely realized due to inherent challenges in welding and joining them. Among the joining methods, solid state techniques are emerging as potential candidates to join MMCs. Having said that, the conventional fusion welding techniques such as GTAW and GMAW can be used to weld MMCs provided suitable care is taken to avoid detrimental reactions. High energy intensity based techniques such as LBW and EBW have good scope for welding joints with good precision and quality. The heterogeneous joining techniques like soldering and brazing have immense potential for joining the industrial components ranging from tool inserts to electronic packaging. Currently, the joining of AMCs is widely studied but Magnesium based MMC are emerging as alternate to AMC and there is a need to explore the joining options and technologies as magnesium possess its own challenges.

References

- Ahearn, J.S., Cooke, C., Fishman, S.G., 1982. Fusion welding of SiC-reinforced Al composites. *Metal Construction* 14 (4), 192–197.
- Assadi, H., Shirzadi, A.A., Wallach, E.R., 2001. *Acta Materialia* 49, 31–39.
- Bassani, P., *et al.*, 2007. Effect of process parameters on bead properties of A359/SiC MMCs welded by laser. *Composites Part A: Applied Science and Manufacturing* 38, 1089–1098. doi:10.1016/j.compositesa.2006.04.014.
- Bhalla, A.K., Williams, J.D., 1977. Production of stainless steel wire-reinforced aluminium composite sheet by explosive compaction. *Journal of Materials Science* 12 (3), 522–530. doi:10.1007/BF00540277.
- Bhattacharyya, D., Bowis, M.E., Gregory, J.T., 1992. The influence of alumina microsphere reinforcement on the mechanical behavior and weldability of a 6061 aluminum metal matrix composite. In *Proceedings of the Conference on Machining of Material Composite, Materials Symposium*. Chicago: ASM Materials Week, p. 49.
- Bouzegzi, N., *et al.*, 2018. Microstructural and electrochemical study of a brazed WC based metal matrix composite obtained by infiltration process. *Journal of Alloys and Compounds* 759 (May), 22–31. doi:10.1016/j.jallcom.2018.05.141.
- Campbell, F.C., 2011. *Manufacturing Technology for Aerospace Structural Materials*. India: Elsevier Inc, Butterworth-Heinemann.
- Ceschini, L., *et al.*, 2010. A study on similar and dissimilar linear friction welds of 2024 Al alloy and 2124Al/SiC P composite. *Advanced Materials Research* 91, 461–466. doi:10.4028/www.scientific.net/AMR.89-91.461.
- Chen, X.G., Da Silva, M., Gougeon, P., St-Georges, L., 2009. Microstructure and mechanical properties of friction stir welded AA6063–B₄C metal matrix composites. *Materials Science Engineering A* 518, 174–184.
- Clyne, T.W., Withers, P.J., 1993. *An Introduction to Metal Matrix Composites*. Cambridge Solid State Science Series. Cambridge University Press. p. 359.
- Dahotre, N.B., McCay, M.H., McCay, T.D., Gopinathan, S., Allard, L.F., 1991. Pulse laser processing of SiC/Al-alloy metal matrix composite. *Journal of Material Research* 6 (3), 514–529.
- Dai, J., *et al.*, 2019. Laser welding of dissimilar metal joint of 6061 Al alloy and Al matrix composite. *Advances in Materials Science and Engineering* 2019, 1–7. doi:10.1155/2019/2359841.
- Dinwoodie, J., Moore, E., Langman, C.A.J., Symes, W.R., 1985. The properties and applications of short staple alumina fibre reinforced aluminium alloys. In: Harrigan, W.C., Strife, J., Dhingra, A.K. (Eds.), *Proceedings of the 5th International Conference on Composite Materials – ICCM-V*. Warrendale, PA: Metallurgical Society of AIME, pp. 671–685.
- Dongdong, Z., *et al.*, 2019. Brazing of Ti-48Al-2Cr-2Nb and TiC/Ti matrix composite using Ag-28Cu filler alloy. *Results in Physics* 14 (78), doi:10.1016/j.rinp.2019.102436.
- Donomoto, T., Funatani, K., Miura, N., Miyake, N., 1983. Ceramic Fibre Reinforced Piston for Performance Diesel Engines. Detroit, MI: SAE Tech. (Paper 830252).
- Ellis, M.B.D., 1996. Joining of aluminium based metal matrix composites. *International Materials Reviews* 41 (2), 41–58.
- Ellis, M.B.D., 2007. Joining of Al-based metal matrix composites – A review. *Materials and Manufacturing Processes* 11, 37–41. doi:10.1080/10426919608947460.
- Enis, M.B.D., 1996. *International Materials Reviews* 41 (2), 41–58.
- Ernst Mikols, T., Burkhard Haas, U., 2003. United State Patent, Patent No. US6991748B2.
- Fernandez, G.J., Murr, L.E., 2004. Characterization of tool wear and weld optimization in the friction-stir welding of cast aluminum 359 + 20% SiC metal-matrix composite. *Materials Characterization* 52, 65–75.
- Gao, Z., *et al.*, 2016. Vacuum brazing between SiCp/6063 Al MMCs and Fe-Ni alloys. *Engineering Review* 36 (3), 249–254.
- Gittos, M.F., Threadgill, P.L., 1991. Preliminary Studies of Joining Particulate Reinforced Aluminium Alloy Metal Matrix Composites, *Metal Matrix Composites III: Exploiting the Investment*. London: Institute of Materials.
- Gómez de Salazar, J.M., Barrena, M.I., 2002. The influence of Si and Mg rich phases on the mechanical properties of 6061 Al-Matrix composites reinforced with Al₂O₃. *Journal of Materials Science* 37, 1497.
- Gülenc, B., *et al.*, 2015. Production of wire reinforced composite materials through explosive welding. *Archives of Civil and Mechanical Engineering* 16, 1–8. doi:10.1016/j.acme.2015.09.006.
- Guo, J., Gougeon, P., Chen, X., 2012. Composites: Part B study on laser welding of AA1100-16 vol% B₄C metal – Matrix composites. *Composites Part B* 43 (5), 2400–2408. doi:10.1016/j.compositesb.2011.11.044.
- Haider, M., El-meligy, M.A., Ali, J., 2019. Investigation on friction stir welding of hybrid composites fabricated on Al–Zn–Mg–Cu alloy. *Integrative Medicine Research*. 4–11. doi:10.1016/j.jimr.2019.06.033.
- Halpin, J.C., 1984. *Primer on Composite Materials: Analysis* (Revise Ed.). Lancaster, PA: Technomic.
- Holcomb, S., 1991. Effect of spinel formation on mechanical properties of alumina reinforced aluminum composites. In: Avedesian, M.M., *et al.* (Eds.), *Proceedings of the conference. Advanced in Production and Fabrication of Light Metals and Matrix Composites*. Montreal: Canadian Institute of Mining, Metallurgy and Petroleum.
- Huang, R.Y., Chen, S.C., Huang, J.C., 2001. Electron and laser beam welding of high strain rate superplastic Al-6061/SiC composites. *Metallurgical and Materials Transactions A* 32, 2575–2584.
- Humpston, G., Jacobson, D.M., 1993. *Principles of Soldering and Brazing*. Materials Park, Ohio: ASM International, p. 188.
- Klomp, J.T., 1989. *Thermodynamics and Chemistry of Ceramic-Metal Interfaces*. Surfaces and Interfaces of Ceramic Materials. Dufourd, L.C., *et al.* (Eds.), Norwell, MA: Klumwer Academic Publisher, pp. 375–392.

- Laurent, V., Chatain, D., Eustathopoulos, N., 1987. Wettability of SiC by aluminium and AlSi alloys. *Journal of Materials Science*, 22, 244–250.
- Li, Y.Z., *et al.*, 2019. Effect of welding speed and post-weld aging on the microstructure and mechanical properties of friction stir welded B₄Cp/6061Al-T6 composites. *Journal of Materials Processing Technology* 273. doi:10.1016/j.jmatprotec.2019.05.023.
- Lis, A., *et al.*, 2018. Bonding through novel solder-metallic mesh composite design. *Materials and Design* 160, 475–485. doi:10.1016/j.matdes.2018.09.017.
- Liu, Y., *et al.*, 2016. Journal of materials processing technology microstructure and mechanical properties of as-reflowed Sn58Bi composite solder pastes. *Journal of Materials Processing Technology* 238, 290–296. doi:10.1016/j.jmatprotec.2016.07.040.
- Lloyd, D.J., 1994. Particle reinforced aluminium and magnesium matrix composites. *International Materials Reviews* 39, 1.
- Long, J., *et al.*, 2020. Effects of minor Zr addition on the microstructure and mechanical properties of laser welded joint of Al/SiCp metal-matrix composite. *Journal of Manufacturing Processes* 49, 373–384. doi:10.1016/j.jmapro.2019.12.004.
- Lu, J., *et al.*, 2012. A new method for soldering particle-reinforced aluminum metal matrix composites. *Materials Science & Engineering B* 177 (20), 1759–1763. doi:10.1016/j.mseb.2012.08.001.
- Maddrell, E.R., 1989. Diffusion Bonding of Aluminium Alloys. PhD Thesis. Cambridge: University of Cambridge.
- Maldonado, C., 1997. Mechanical and metallurgical properties of MMC friction welds. *Welding Journal* 76, 367–373.
- Mallick, P.K., 2016. Composites Engineering Handbook, Part – 2, CRC Handbooks Collection. Boca Raton: CRC Press, Taylor & Francis Group.
- Marzoli, L.M., Strombeck, A.V., Dos Santos, J.F., Gambaro, C., Volpone, L.M., 2006. Friction stir welding of an AA6061/Al₂O₃/20p reinforced alloy. *Composites Science and Technology* 66, 363–371.
- Meng, C., *et al.*, 2013. Evolution behavior of TiB₂ particles during laser welding on aluminium metal matrix composites reinforced with particles. *Transactions of Nonferrous Metals Society of China* 23, 1543–1548. doi:10.1016/S1003-6326(13)62628-X.
- Nicholas, M.G., 1989. Metal-Ceramic Interfaces. *Surfaces and Interfaces of Ceramic Materials*. Dufourd, L.C., *et al.* (Eds.), Norwell, MA: Kluwer Academic Publisher. pp. 394–417.
- Niu, J., *et al.*, 2006. Research on laser welding of aluminum matrix composite SiCw/6061. *Vacuum* 80 (11–12), 1396–1399. doi:10.1016/j.vacuum.2006.01.023.
- Niu, J., Lai, Z., Wang, M., Liu, L., Wu, L., 2001. *Journal of Materials Science and Technology*. (1), 173–174.
- Niu, J., Zhang, D., Ji, G., 2003. *Transactions of Nonferrous Metals Society of China* 13, 289–291.
- Park, J.K., Lucas, J.P., 1997. Moisture effect on SiCp/6061 Al MMC: Dissolution of interfacial Al₄C₃. *Scripta Materialia* 37, 511–515.
- Partridge, P.G., Dunford, D.V., 1991. *Journal of Materials Science*. 26, 2255.
- Ramli, M.I.I., *et al.*, 2016. Effect of TiO₂ additions on Sn-0.7Cu-0.05Ni lead-free composite solder. *Microelectronics Reliability* 65, 255–264. doi:10.1016/j.microrel.2016.08.011.
- Salazar, D., Barrena, M.I., 2003. Dissimilar fusion welding of AA7020/MMC reinforced with Al₂O₃ particles. Microstructure and mechanical properties. *Materials Science and Engineering A* 352, 162–168.
- Shin, D.S., Lee, J.C., Yoon, E.P., Lee, H.I., 1997. Effect of the processing methods on formation of Al₄C₃ in SiCp/2024 Al composites. *Materials Research Bulletin* 32, 1155–1163.
- Shirzadi, A.A., Assadi, H., Wallach, E.R., 2001. Interface evolution and bond strength when diffusion bonding materials with stable oxide films. *Surface and Interface Analysis* 31, 609–618. doi:10.1002/sia.1088.
- Shirzadi, A.A., 1998. Diffusion Bonding Aluminium Alloys and Composites: New Approaches and Modelling (Doctoral thesis). doi:10.17863/CAM.14221.
- Srinath, M.S., Sharma, A.K., Kumar, P., 2011. A new approach to joining of bulk copper using microwave energy. *Materials and Design* 32 (5), 2685–2694. doi:10.1016/j.matdes.2011.01.023.
- Stacey, M.H., 1988. Production and characterization of fibres for metal matrix composites. *Materials Science and Technology*. 4, 227.
- Sugiyama, Y., 1989. Brazing of aluminum alloys. *Welding International Journal* 8, 700–710.
- Ureña, A., *et al.*, 2001. High temperature soldering of SiC particulate aluminium matrix composites (series 2000) using Zn–Al filler alloys. *Science and Technology of Welding and Joining* 6 (1), 1–11. doi:10.1179/136217101101538479.
- Ureña, A., Gomez De Salazar, J.M., Escalera, M.D., Fernandez, M.I., 1997. Study of the brazability of aluminum matrix composites. *Welding Journal*. 92–102.
- Ureña, A., Escalera, M.D., Gil, L., 2000. *Composites Science and Technology* 60, 613–622.
- Viala, J.C., Bosslet, F., Laurent, V., Lepetitcorps, Y., 1993. Mechanism and kinetics of the chemical interaction between liquid aluminium and silicon-carbide single crystals. *Journal of Materials Science* 28, 5301–5312.
- Vijay, S.J., Murugan, N., 2010. Influence of tool pin profile on the metallurgical and mechanical properties of friction stir welded Al-10 wt% TiB₂ metal matrix composite. *Materials and Design* 31 (7), 3585–3589. doi:10.1016/j.matdes.2010.01.018.
- Viot, A., Gunnick, J.W., 2001. *Fibre Metal Laminates an Introduction*. Kluwer Academic Publishers.
- Wang, H.M., Chen, Y.L., Yu, L.G., 2000. In-situ weld-alloying/laser beam welding of SiCp/6061Al MMC. *Materials Science and Engineering A* 293, 1–6.
- Wang, X.H. J.-t., Niu, J.T., Guan, S.K., Wang, L.J., Cheng, D.F., 2009. *Materials Science and Engineering A* 499, 106–110.
- Wei, C., *et al.*, 2018. Microstructure and mechanical performance of composite joints of sapphire by ultrasonic-assisted brazing. *Journal of Materials Processing Technology* 257 (92), 1–6. doi:10.1016/j.jmatprotec.2018.02.011.
- Weis, S., Hoyer, I., Wielage, B., 2008. Joining of high-strength aluminum-based materials with tin-based solders. *Welding Journal*. 35–37.
- Wert John, A., 2003. Microstructures of friction stir weld joints between an aluminium-base metal matrix composite and a monolithic aluminium alloy. *ScriptaMaterialia* 49, 607–612.
- Xi-he, W., *et al.*, 2009. Investigation on TIG welding of SiCp-reinforced aluminum-matrix composite using mixed shielding gas and Al-Si filler. *Materials Science and Engineering A* 499 (1–2), 106–110. doi:10.1016/j.msea.2008.07.037.
- Xu, Z., *et al.*, 2012. Composites: Part A wetting and oxidation during ultrasonic soldering of an alumina reinforced aluminum – copper – magnesium (2024 Al) matrix composite. *Composites Part A* 43 (3), 407–414. doi:10.1016/j.compositesa.2011.12.006.
- Yan, J.C., *et al.*, 2008. Vibration assisted brazing of SiCp/A356 composites: Microstructure and mechanical behaviour. *Science and Technology of Welding and Joining* 13 (8), 760–764. doi:10.1179/136217108 × 333318.
- Yu, Z.S., Li, R.F., Qi, K., 2010. Joining of SiC particle reinforced aluminium metal matrix composites by electromagnetic field aided brazing method. *Materials Science and Technology* 26 (6), 695–698. doi:10.1179/174328409 × 430546.
- Yue, T.M., Xu, J.H., Man, H.C., 1997. Pulsed Nd-YAG laser welding of A SiC particulate reinforced aluminium alloy composite. *Applied Composite Materials* 4, 53–64.
- Zhai, Y., North, T.H., 1997. *Journal of Materials Science* 32, 5571.
- Zhou, N., *et al.*, 2014. Experimental and numerical study on the ballistic resistance of steel-fibre reinforced two-layer explosively welded plates. *Materials and Design* 54, 104–111. doi:10.1016/j.matdes.2013.08.022.

High Performance Machining of Metal Matrix Composites

Keng S Woon, National University of Singapore, Singapore

© 2021 Elsevier Inc. All rights reserved.

Introduction

Metal matrix composite (MMC) is a marvel of modern engineering. By reinforcing a base metal alloy with intermetallic compounds in the form of particles, whiskers or continuous filaments, mechanical properties of MMCs like yield strength, tensile strength, fatigue strength, elastic modulus, thermal shock, etc. [Kainer \(2006\)](#) become far more superior than the base alloy alone. Thus, MMCs are now used in a much wider context – from advanced space shuttles, fuel-saving automobiles to cost-effective sports equipment since they were first introduced to the aviation industry half a century ago. Most of these applications aim to promote specific strength and stiffness, high-temperature strengths and wear resistance ([Taya and Arsenault, 1989](#)). But one man's meat is another man's poison. Due to the superior mechanical properties as a whole and localized abrasive nature of the intermetallic reinforcements in MMCs, cutting tools usually degrade rapidly during machining, which indicates drastic reduction in the machinability of MMCs ([Everett and Arsenault, 1991](#)). Many studies in the past focused on the effects of the latter.

According to [Weinert \(1993\)](#), the rapid tool wear on both rake and clearance faces is mainly due to direct abrasion of the reinforcements during chip formation and surface generation and deduced that hardness of reinforcement and relative sliding motion between cutting tools and reinforcements are among the main factors. This was supported by a study on the effects of cutting conditions conducted by [Tomic and Tonnessen \(1992\)](#) where they determined severe flank wear on cutting tools corresponds closely to high cutting speeds due to abrasive wear. High feed rates, on the contrary were found to help in preserving tool life and reducing wear. [Li and Seah \(2001\)](#) described such tool wear mechanism as a combination of two-body and three-body abrasion where tool flank face is plowed by reinforcement particles within the metal matrix as well as those dislodged from the matrix. This theory explains the rapid acceleration in abrasive tool wear when the weight percentage of reinforcement exceeds a critical threshold due to mutual interaction between reinforcement particles that eventually resulted in a catastrophic interference. Other than the effects of volume percentage, [Lane \(1992\)](#) also studied size effects of the reinforcement within MMCs. It was reported that a 27% diametric reduction of particulate reinforcement can lead to a 500% improvement in tool life while a 50% decrease in volume percentage of the reinforcement can only improve tool life by 21%. In a separate study, [Gergman and Jacobson \(1994\)](#) also found fine reinforcements in whisker form cause significantly less abrasive wear on the rake face as compared to the relatively bigger reinforcements in the shape of particulate. They claimed that fine whiskers are fragmented by shearing at the primary deformation zone during chip formation.

Surface generation in machining is carried out with the use of physical cutting tools, with precise and well-defined geometries to remove materials mechanically through the formation of chips. Chips are formed through shearing and plastic deformation when the strength of workpiece materials is overcome by the advancing cutting tools at designated cutting parameters and a new surface is simultaneously generated. Through such a mechanical process, topography of the surface and its quality is governed by the tool conditions. But when wear is developed rapidly on cutting tools, tool geometries are altered correspondingly at the same rate, and over time they become greatly deviated from the original design. As a result, the surface topography and surface quality produced are impaired because drastic alteration in tool geometries changes the mechanics of chip formation and surface generation. With the hard and brittle reinforced inclusions, the resultant surface conditions are even more complex. In the machining of Al/SiC_p 20 wt%, [El-Gallab and Sklad \(1998\)](#) found SiC particles are pulled-out of the surface or experienced interfacial debonding, leaving behind voids and scratches while the remaining ones are fractured through secondary crack initiation by plastic deformation within the metal matrix. The use of average surface roughness (Ra) to describe surface qualities of this sort is less presentative as the voids and scratches are highly localized. [Ge et al. \(2008\)](#) observed an improvement in surface finish with SiC particles are pressed back into the surface through careful control of the cutting process although microstructures on the machined surface are inevitably deformed. The findings were reported following a study using monocrystalline diamond tools on an ultraprecision lathe machine. With similar observations, [Kannan and Kishawy \(2006\)](#) revealed significantly greater hardness closer to machined surface than the subsurface as a result of work-hardening induced plastic deformation. The plastic zone is deeper on softer metal matrix and vice versa, which implies the effects of particle weight/volume fraction and size on the intensity of subsurface deformation.

The selected few studies above represent two decades of intense research to identify the reasons behind low machinability, the causes of tool wear as well as the difficulties to yield admirable surface finish in MMC machining. This article aims to render a pragmatic discussion on the methods and strategies to promote the machining performance of MMC. The first section provides a detailed description of the cutting process where the unique tool wear mechanism in MMC machining that limits tool life, surface finish, productivity and the overall performance is governed by the modes of interaction between the cutting tools and the reinforced particles within the matrix. Once the root cause of the challenge is clarified, a comprehensive 3-part solution for high performance machining of MMCs is proposed namely: tool materials, cutting fluid and vibration-assisted machining. So, in the second section, the types of commercial tool materials that are proven feasible in machining MMCs are examined and detailed as a guidance for decision making in the shop floor. A sub-section on economic factors and justifications is included in view of the

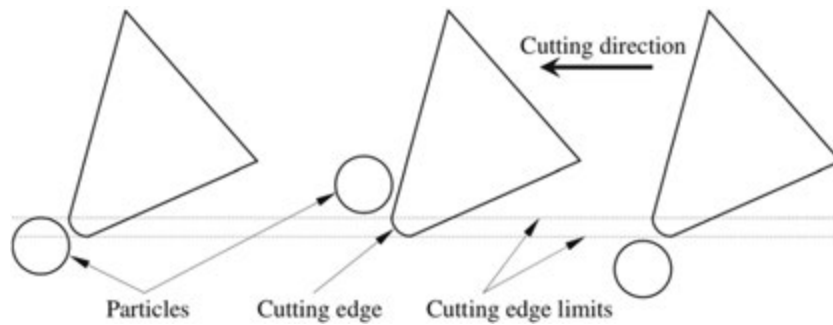


Fig. 1 Tool-particle contact configuration along, above or below the tool path. Reproduced from Pramanik, A., Zhang, L.C., Arsecularatn, J.A., 2007. An FEM investigation into the behavior of metal matrix composites: Tool-particle interaction during orthogonal cutting. *International Journal of Machine Tools & Manufacture* 47, 1497–1506.

importance of cost effectiveness. After the decision on tool materials is made, the next step is to develop an effective cutting fluid strategy. Therefore, the third section focuses on the evaluation of various cutting fluids and delivery methods with considerations of the peculiar cooling, lubrication and chip breaking requirements. Finally, in the last part, a high-performance machining solution for MMCs using vibration-assisted machining is discussed as it has great advantage to increase productivity, improve surface finish and save energy.

The Cutting Process

A complete description of the mechanism behind MMC machining involves the matrix deformation and interactions between the cutting tool and reinforcement particles. From a statistical possibility viewpoint, the cutting edge of a tool will encounter a reinforcement particle either along, above or below the tool path during machining as shown in Fig. 1. According to Pramanik *et al.* (2007), the contact and deformation mechanics derived from these interactive configurations give rise to tool wear, surface damage and particle debonding during MMC machining.

Consider incremental stages of a typical machining operation of particulate reinforced MMC by means of von Mises strain evolution illustrated in Fig. 2(a)–(f). In the beginning when the tool advances into the MMC workpiece, the matrix is deformed in bulk by the rake face and shearing takes place along the primary deformation zone. Further advancement of the tool will eventually meet a particle at the cutting edge and cause it to debond from the matrix. The hard particle is loose and thus unlikely to be sheared by the cutting edge but as it remains on the machined surface, the flank face of the passing tool will plow against it and induces plastic deformation on the matrix around its vicinity. Eventually the debonded particle is dislocated from the matrix entirely – leaving behind cracks and pit holes on the machined surface due to particles dislocation and plowing as shown in Fig. 3.

Meanwhile, the chip produced simultaneously as the matrix is severely deformed climbs on to the rake face and establishes the secondary shear zone. Through such tribological interactions, particles above the tool path will begin to debond as the chip climbs along the rake face continues to grow in size. Eventually most of the particles that come into direct contact on the rake face are debonded entirely towards the end of the secondary shear zone while some will still be remained in the chip. On the other hand, particles below the tool path do not come into direct contact with the tool and therefore will not be deformed but they are pressed further into the machined surface akin to a micro-indentation process (Pramanik *et al.*, 2006) and resulted in a strained or work-hardened layer in the subsurface of the matrix. Fig. 4 shows the depth of such work-hardened layers in two different aluminum MMCs after machining.

The intermetallic reinforcements used in MMCs be it carbide, oxide or nitride are very hard and highly abrasive. The numerical results in Fig. 2 with excellent microscopic details confirm that the cyclical plow engagement of these reinforcing particles contributes mainly to crater and flank wear development on the cutting edge (Fig. 5(a)). To some greater extent with reinforcement particles that are relatively larger in size and/or weight percentage above some critical threshold, deep grooves or notches (Fig. 5(b)) and intergranular fracture (Fig. 5(c)) on the flank faces are produced. In conjunction with the use of high cutting speeds, the cutting edge can undergo a complete catastrophic fracture (Fig. 5(d)) associated with thermo-mechanical failures. Wear on the rake face caused by two-body and three-body abrasion of the bonded and debonded particles when chip flows on the rake face is notably less severe as a comparison with the absence of cyclical plowing.

Tool Materials

Material removal in machining is performed with the use of physical cutting tools. The three salient attributes in cutting tools that promote durable usages are: (1) high temperature stability; (2) brittle fracture resistance; and (3) surface deformation resistance. The latter governed by the hardness of tool materials is essential in machining MMCs while preventing accelerated abrasive wear by the

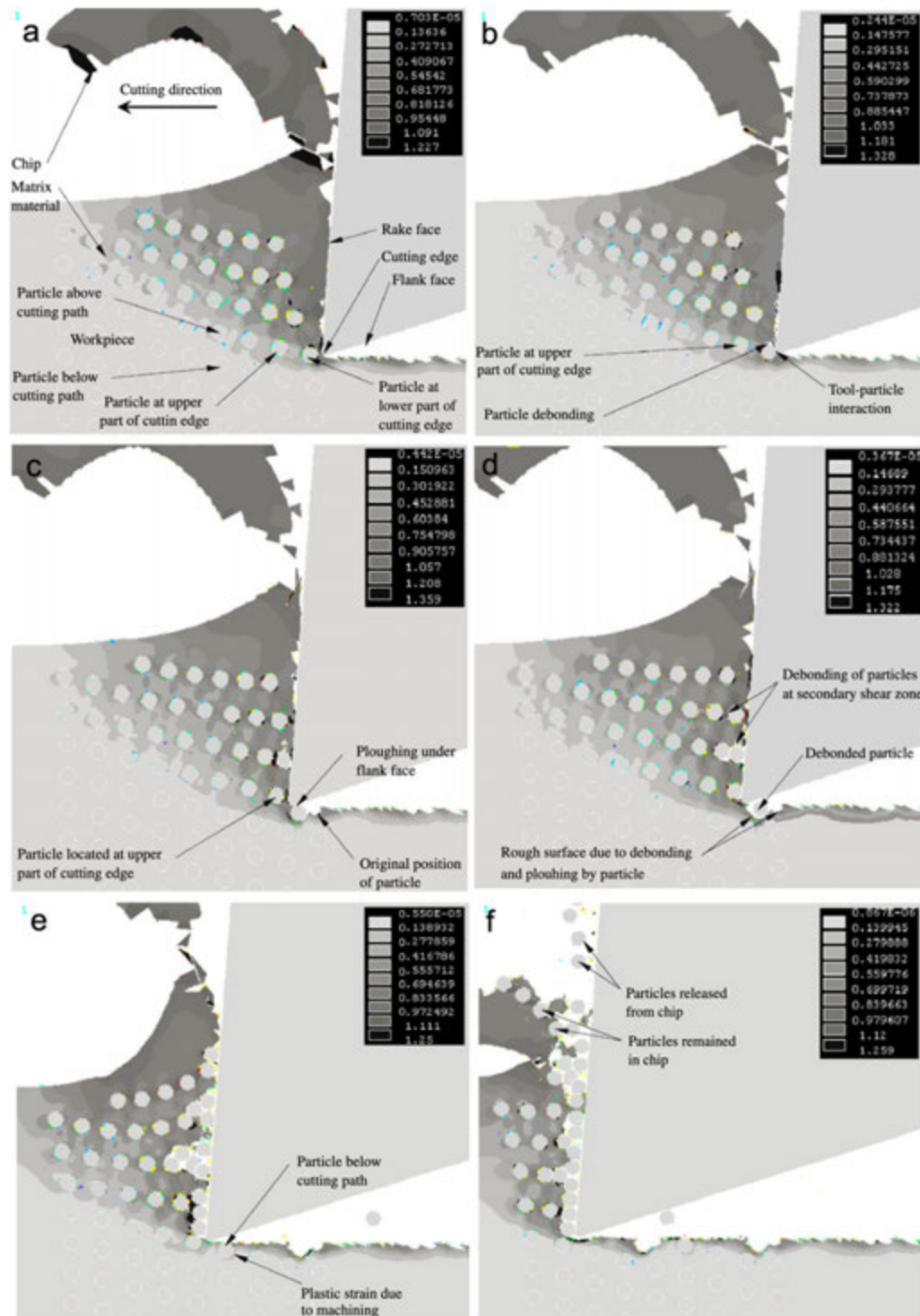


Fig. 2 Evolution of tool-particle contact behavior and von Mises strain. Reproduced from Pramanik, A., Zhang, L.C., Arsecularatn, J.A., 2007. An FEM investigation into the behavior of metal matrix composites: Tool-particle interaction during orthogonal cutting. *International Journal of Machine Tools & Manufacture* 47, 1497–1506.

intermetallic reinforcements. Conventional cemented carbides are usually limited to roughing purposes (Teti, 2002) by leveraging on the good balance between toughness and hardness to remove bulk materials without over emphasis on surface quality and dimensional accuracy. This is largely because tungsten carbide grains in cemented carbide tools are not much harder than intermetallic reinforcement particles like silicon carbide and alumina and therefore concentrated loading in finish machining will lead to rapid development of localized tool wear. Diamond coatings attempted in the past (Chou and Liu, 2005; Kremer *et al.*, 2008; Wang *et al.*, 2010) to improve

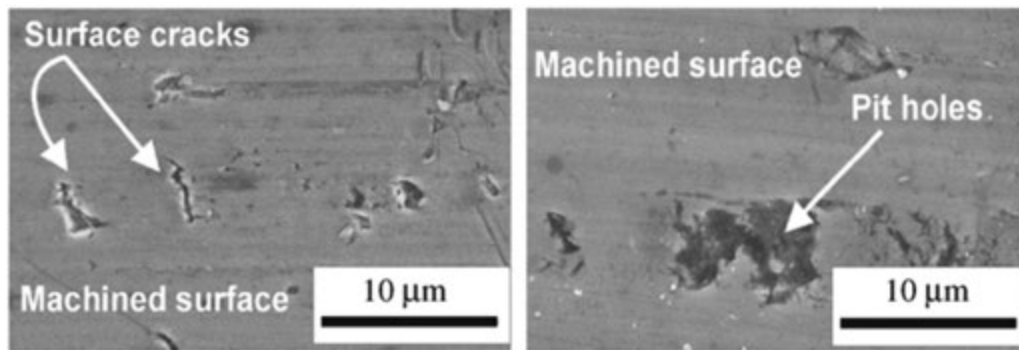


Fig. 3 Common surface defects including cracks and pit holes on machined surface. Reproduced from Kannan, S., Kishawy, H.A., 2006. Surface characteristics of machined aluminium metal matrix composites. *International Journal of Machine Tools & Manufacture* 46, 2017–2025.

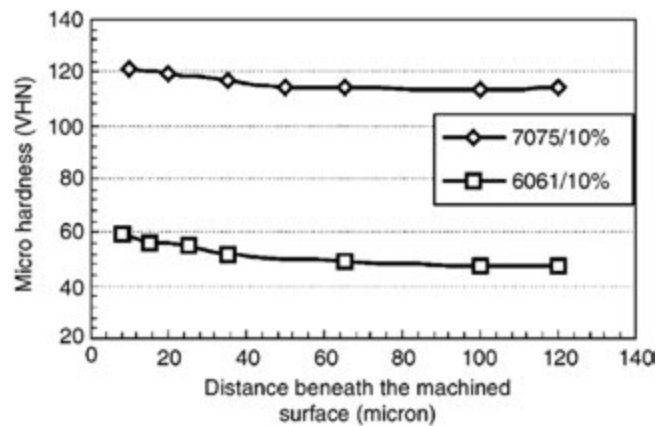


Fig. 4 Microhardness variation in aluminum MMCs due to work-hardening. Reproduced from Kannan, S., Kishawy, H.A., 2006. Surface characteristics of machined aluminium metal matrix composites. *International Journal of Machine Tools & Manufacture* 46, 2017–2025.

resistance against abrasion did not gain reasonable success as surface coatings are prone to fail under intense loading. With hardness as the priority, two commercial tool materials can still be considered: (1) polycrystalline diamond (PCD); and (2) cubic boron nitride (CBN).

PCDs are synthetic diamonds reproduced based on mankind's understanding of natural diamonds – the hardest and one of the most valuable materials on earth. Natural diamonds were formed deep underground, up to 700 km from the surface of the earth where pure carbon is crystalized in very strong cubic structures the under optimal conditions of high pressures and high temperatures (HPHT) several millions of years ago. Thus, these precious stones are scarce and too costly for machining operations despite the excellent hardness of up to 10 Mohs (Klein, 2007) is most ideal to resist abrasive wear. This has inspired intense research and by 1955, the first synthetic diamond coined as PCD was produced from graphite by General Electric in USA with an optimized HPHT process. Using a similar method, CBN is synthesized from a polycrystalline mass consists of boron and nitride and the resultant hardness is only superseded by diamonds. CBN has since been used successfully in special machining applications. Primarily, a selected group of materials primarily made up of iron-, nickel-, cobalt-based alloys (Oya and Otani, 1979) that cannot be handled with PCD tools due to chemical solubility at high temperatures. The feasibility of using PCD and CBN for MMC machining was previously validated alongside with conventional tooling like high speed steel (HSS), coated HSS, cemented carbide (WC) and coated WC.

Fig. 6 shows the collective tool life and cutting speed results tested on cast and powder-formed aluminum-based composites reinforced with 20 wt% silicon carbide particles adapted from Hung *et al.* (1995). As tool life is governed by abrasive wear in MMC machining, the performance ranking that goes by hardness differences among tool materials is logically expected. PCD and CBN tools are consistently more superior than other tool materials due to superiority in surface hardness and such superiorities are linearly proportional to hardness as summarized in Table 1. At comparable cutting speeds, PCD tools can outlast coated and uncoated WC tools by two scale order of tool life in minutes and around a scale order compare with CBN tools. HSS tools perform very poorly in machining MMC and therefore should not be considered entirely. It is also worth noting that the usefulness of surface coatings is very limited, be it on WC or HSS the life span of cutting tools will be governed by coating conditions when they are coated. Once coatings are failed by peeling or chipping, the tools can no longer be used because cutting loads generated from the process and particles abrasion will be highly concentrated on the coating failure sites, resulted in accelerated degradation and

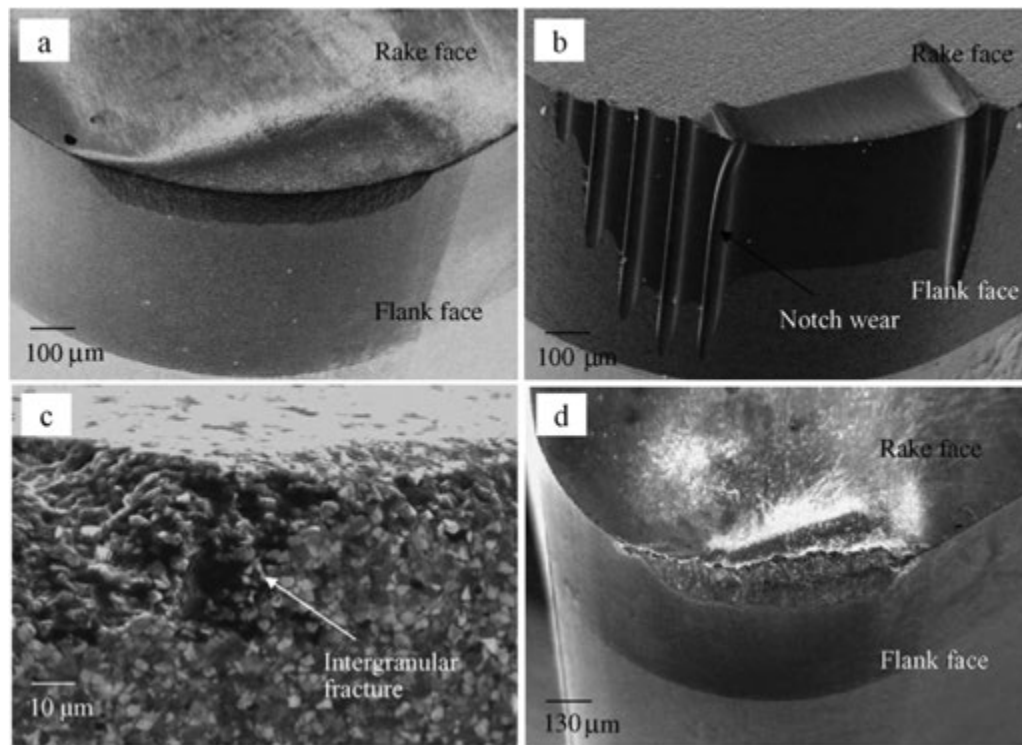


Fig. 5 Typical defects on cutting tools: (a) rake and flank wear; (b) notching; (c) intergranular fracture; and (d) catastrophic fracture. Reproduced from Ding, X., Liew, W.Y.H., Liu, X.D., 2005. Evaluation of machining performance of MMC with PCBN and PCD tools. *Wear* 259, 1225–1234.

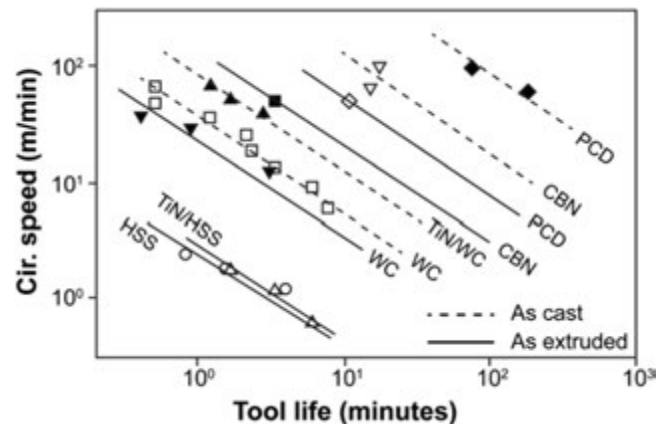


Fig. 6 Tool life-cutting speed plot for various tool materials in machining cast and extruded aluminum MMCs. Reproduced from Hung, N.P., Boey, F.Y.C., Khor, K.A., Oh, C.A., Lee, H.F., 1995. Machinability of cast and powder-formed aluminum alloys reinforced with SiC particles. *Journal of Materials Processing Technology* 48, 291–297.

then catastrophic fracture. This phenomenon is especially prominent for milling and drilling where cutting is performed intermittently.

Despite the superiority of PCD as depicted in Fig. 6, there is a speed limit in how fast PCD tools are used for MMC machining due to the formation of built-up edge (BUE). High cutting speed generates large amount of heat through friction and shearing during chip formation. A large fraction of the heat is taken by the PCD tools due to the high thermal conductivity of diamonds. The remaining is carried away by the chip and transferred into the workpiece through conduction. At high cutting speeds, the workpiece is readily heated up and resulted in thermal softening of the work materials adjacent to the cutting edge. In the subsequent cycles of cutting, these materials are deposited onto the tools and built up continuously under a combination of enabling localized pressure and temperature. Fig. 7 shows a sample of BUE on PCD tools and its x-ray dispersion profile. Though BUE can reduce abrasive wear on the cutting edge momentarily, it is an unstable two-phase compound that breaks down

Table 1 Hardness of selected tool materials

Material	Knoop hardness (1N, 15 s)
PCD	7000
CBN	3800
SiC	2500
WC	2100
TiN	1770
HSS	980

Note: Reproduced from Hung, N.P., Boey, F.Y.C., Khor, K.A., Oh, C.A., Lee, H.F., 1995. Machinability of cast and powder-formed aluminum alloys reinforced with SiC particles. *Journal of Materials Processing Technology* 48, 291–297.

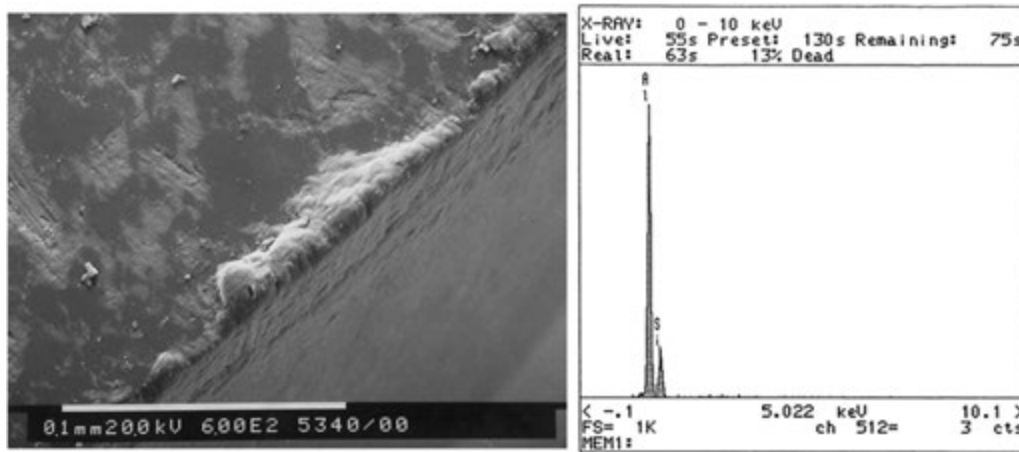


Fig. 7 Development of built-up edge on PCD tools and its x-ray dispersion profile Reproduced from El-Gallab, M., Sklad, M., 1998. Machining of Al/SiC particulate metal matrix composites Part II: Workpiece surface integrity. *Journal of Materials Processing Technology* 83, 277–385.

unpredictably when its size gets bigger. Through a vicious cycle of building up and breaking down, BUE brings about deterioration in part accuracy and surface finishing and therefore should be prevented in machining.

From the results above, it is noteworthy that metal matrix composites are considered as difficult-to-machine materials (Barnes and Pashby, 1995) due to its highly abrasiveness. Therefore, it is vital for manufacturing engineers to deploy the right type of tool materials to avoid premature tool failure and frequent machine down. But there is a fuller picture to consider when it comes to making this decision – economic factors and justifications of the manufacturing operation. Tool life aside, different tool materials operate at different ranges of speed, feed and depth of cut which determine the material removal rates and productivity of the process. While it is tempting to use PCD and CBN tools for every machining need and scenario, the cost of these tooling may not be economically feasible for the whole operation. A decision on tool materials is thus best made with a mindful balance between cost and productivity.

In the economics of machining, an economy index E can be derived for each tool material as reference based on the type of machining operation, by considering the cost per cutting edge M and the material removal rate Q : $E=M/Q$ (Hung *et al.*, 1995). **Table 2** illustrates the economy indexes for a range of tool materials for a facing operation. Lower E values indicate a more economical process and vice versa. Exploring a cost-effective solution based on the economy index, it is recommended that MMCs should be subjected to rough machining with uncoated WC tools and followed by finishing cut with PCD tools.

Cutting Fluids

Cutting fluid is used in machining as performance-enhancing agents. In general, these fluids are specially designed to serve two primary purposes: (1) remove heat generated from frictional heating and shear heating during chip flow and material deformation; (2) reduce coefficients of friction at tool-chip and tool-work interfaces; and a secondary purpose: (3) facilitate in the breaking of chips into small segments for evacuation and disposal. It is usually supplied directly to the cutting zone, as close to the cutting edge as possible where chip formation takes place. In most scenario, cutting fluids are delivered at high pressure to break and flush the chips away from the cutting zone. When chips are broken down and removed efficiently, the access of cutting fluid to

Table 2 Indicative economy index of selected tool materials in machining MMCs

MMC	Cutting tool	HSS, TiN/HSS	WC	TiN/WC	CBN	PCD
Powder-formed	Cutting speed (m/min)	0.42	3.5		21	55
	Relative speed	1	8.3		50	131
	Economy index (US\$ min/cm ³ /edge)	510	6.9		204	104
Cast	Cutting speed (m/min)		5.5	13	131	572
	Relative speed		13	31	312	1362
	Economy index (US\$ min/cm ³ /edge)		4	5	33	10

Note: Reproduced from Hung, N.P., Boey, F.Y.C., Khor, K.A., Oh, C.A., Lee, H.F., 1995. Machinability of cast and powder-formed aluminum alloys reinforced with SiC particles. *Journal of Materials Processing Technology* 48, 291–297.

the cutting edge is improved so that the intended cooling and lubrication effects are realized. For hole-making operations with restrictive fluid access from the outward, through-spindle systems are used to deliver cutting fluids through internal conduits of the spindles through the drills and then the cutting edges. Therefore, successful application of cutting fluids can help in regulating cutting temperatures and alleviating frictional contact. As a result, thermo-mechanical wear on cutting tools is minimized, tool life is prolonged and machining performance is enhanced, which can be indicated from reductions in cutting force and cutting energy as well as improvements in surface finishing and dimensional accuracy.

Cutting fluids are formulated according to the two primary purposes. For heat removal, water-based cutting fluids with high specific heat and thermal conductivity (Groover, 2017) known as coolants are proven effective. For friction reduction, on the other hand, oil-based cutting fluids or lubricants that form lubricating thin-films at the tool-chip and tool-work interfaces are used. Coolants are applied in machining processes and applications such as turning and milling of stainless steels that require high cutting speeds or when thermally vulnerable tool materials such as high speed steel or uncoated cemented carbide are in use. Under these conditions where aggressive heat generation or severe thermal damage is inevitable, the use of coolant helps to remove intense heat from cutting tools and workpieces through conduction so that cutting temperatures are kept at operational safe, and non-alarming levels. On the contrary, lubricants are usually used in low cutting speed applications like broaching, tapping or drilling. These oil-based cutting fluids are formulated with extreme pressure (EP) additives like organic sulfur, phosphorous or chlorine compounds, which chemically establish thin films on the cutting tools under high, localized pressures at the contact interfaces. These thin films with thicknesses ranging in the micrometer and nanometer scales are maintained on cutting tools at low cutting speeds and keep them from continuous direct contact with chips and workpieces. Through this mechanism, the lubricated cutting tools are subjected to lesser friction and hence mechanical abrasion and frictional heating are also reduced correspondingly.

Commercial cutting fluids are typically classified in 3 categories: (1) cutting oils; (2) emulsions; and (3) synthetic/semisynthetic fluids. Cutting oils are developed from petroleum, animal, vegetable, and fish in conjunction with a careful blend of EP additives, oxidation inhibitors, rust preventatives, antiseptics, odor control agents and anti-foaming agents (Groover, 2017). Cutting oils have superior lubricating properties due to their strong adhesion on metallic surfaces as well as their high viscosities, which allow the formation of effective thin-films with large thicknesses compare with those of water-based fluids. As a result, the impact of frictional contact during machining is greatly minimized. But thermal conductivity and specific heat of cutting oils are relatively low and thus the capability to cool is weak. To improve cooling capabilities in cutting fluids, water being one of the best cooling medium is essential. For applications that call for both effective cooling and lubrication, mineral oils blended in water known as emulsions or emulsifiable oils can be considered. Emulsions combine mineral oils in water at designated proportions and stabilized with emulsifying agents to disintegrate oils into droplets alongside with EP additives to enhance the lubricating effects under high localized pressures. Commercial emulsions are custom made from mixing 1–5 parts of emulsifiable oil in 100 parts of water (Fiytzpatrick and Smith, 2019) to cater for varying levels of cooling and lubrication requirements in an application. To maximize cooling effects, synthetic fluids that are 100% water-based and chemically enhanced with inorganic chemicals including blending agents, rust prevention agents and anti-bacteria agents are used. Certain EP additives like phosphorous, chlorine and sulfur compounds are also incorporated to promote some levels of lubrication and friction reduction. If more lubrication properties are desirable, small amount of emulsifiable oils are added into synthetic fluids. These cutting fluids are marketed as semisynthetic fluids. On top of these conventional options, the use of liquid nitrogen as cutting fluid to improve tool life and machining performance has been an on-going research (Shokrani et al., 2012).

Consider a comprehensive feasibility study (Duan et al., 2019) on the cooling and lubrication effectiveness of different cutting fluids and supply conditions: (1) Oil: Flooding neat cutting oil at 36 l/h; (2) Emulsion: Flooding a blend of oil to water ratio 1:10 at 36 l/h; (3) MQL: Minimum quantity lubrication is delivered as mist with a mixture of oil and pressurized gas at 0.4 MPa that consumes oil at 83 ml/h; (4) LN₂: Liquid nitrogen with a calibration temperature of –165°C and delivered at 0.4 MPa. (5) Dry: Machining is performed without cutting fluids. Silicon carbide particle reinforced aluminum matrix composites (Al/SiC_p 50 wt%) are subjected to turning with PCD tools at a cutting speed 120 m/min, feed rate 0.1 mm/rev and depth of cut 0.2 mm for a uniform distance of 1375 m. Synthetic fluids are not used in the study as the tool wear mechanism is mainly driven by frictional contact of the particle reinforcements. Abrasive wear is a direct product of such wear mechanism due to mechanical abrasion while

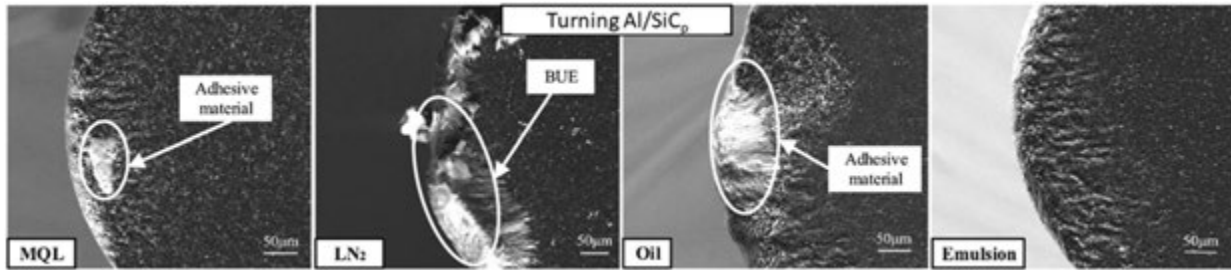


Fig. 8 Built-up edges and adhesive materials found on rake faces except emulsion application. Reproduced from Duan, C., Sun, W., Che, M., Yin, W., 2019. Effects of cooling and lubrication conditions on tool wear in turning of Al/SiCp composite. *The International Journal of Advanced Manufacturing Technology* 103 (1–4), 1467–1479.

subsequent sliding contact heats up both cutting tool and workpiece. When the heated surfaces come into contact, thermally softened workpiece is adhered on cutting tools under high localized pressures and form unstable build-up edges (BUEs) over the cutting edges. As cutting goes on, BUE continues to grow in size until a saturated stage is reached where it will be detached either partially or entirely from the cutting tool and leave a tear mark behind known as adhesive wear. As shown in **Fig. 8**, the study found BUEs and traces of adhesive wear for all cutting with MQL, LN₂, Oil except Emulsion. This implies neither extreme cooling nor lubrication, but a balance between the two can suppress the formation of BUEs and prevent adhesive wear in MMC machining.

Fig. 9 shows the flank wear (VC) at different stages of the same feasibility study. As discussed previously in Section “The Cutting Process”, flank wear in MMC machining is mainly caused by mechanical abrasion of the reinforced particle. From the results (Duan *et al.*, 2019), the best flank wear performance was achieved under LN₂ and MQL conditions while on the contrary, the used of emulsion and neat cutting oil produced the worst. It is believed that the highly tight contact established between flank face and workpiece during machining restricts the access of unbonded particles. Therefore, the use of flooding methods to deliver emulsion and oil to the cutting edge for flushing and evacuation of loose particles does not produce visible improvements. Worse still, supplying cutting fluids to the tools that are already heated up through frictional heating and plastic deformation leads to formation of vapor pockets around the tool, which restricts the access of lubricant and thus resulted in severe abrasive wear. The use of LN₂ and MQL has the advantage to eradicate these vapors with the pressurized gas while delivering the cooling and lubricating agents to the narrow flank face zone that improves the frictional conditions and greatly reduces flank wear on cutting tools. Such findings also imply flank wear on cutting tools is primarily induced by 2-body abrasion in MMC machining.

Vibration-Assisted Machining

The challenges in optimizing MMC machining performance is directly related to the challenges in managing wear rate of cutting tools (Muthukrishnan and Davim, 2009). These challenges originate from the on-going interaction between the cutting tools and abrasive particles in MMCs. Unbonded particles trapped between the rake face and the chip bottom coupled with bonded particles in the chips induce severe crater wear on rake face through a complex 3-body abrasion action. Crater wear is aggravated by MMCs with higher weight percentage of reinforced particles in the matrix (Joshi *et al.*, 1999). On the other hand, wear on the flank face is primarily caused by 2-body abrasion of bonded particles on the machined surface after the immediate layer of materials is removed. Such wear on flank face usually deteriorates with intensification in springback or elastic recovery (Quan and Zhou, 2000) by making wrong choices on machining conditions or tool materials. Moreover, applying the right cutting fluids with the right method can suppress wear development on both faces by providing the necessary cooling and lubrication. Otherwise, the use of cutting fluids is counterproductive and a waste of resources.

The central issue of effective cutting fluids application in MMC machining is accessibility. During chip formation, the part of rake face adjacent to the cutting edge is always tightly engaged at the chip root while the remaining is constantly shielded by the forming chip. Similarly, the flank face adjacent to the cutting edge is always adhering against the machined surface despite having a back-grinding clearance angle, owing to the finite tool sharpness. Under these contact conditions, the access to the rake and flank faces by cutting fluids is therefore highly restrictive. To overcome this major issue, cutting tools should be displaced to create enough clearance for cutting fluids to infiltrate both tool faces. If such tool displacement is precisely executed, even if it's just momentarily, the rate of tool wear development can be improved when tool wear is alleviated to a certain degree by instant cooling and lubrication, through successful cutting fluid infiltration. In addition, by displacing the tools disrupt continuous 2-body abrasion on both rake and flank faces and minimize 3-body abrasion on the former by relieving unbonded particles trapped in between chips and rake faces. Once the desirable outcomes are achieved, restore the tools back to the original paths and positions to continue with the intended cutting. By repeating such tool displacement and restoration interchangeably, systematically and at a high level of accuracy, high performance machining of MMCs is readily realized. The feasible machining technology to deliver such peculiar requirements is vibration-assisted machining (VAM).

VAM was originally developed to machine difficult-to-machine materials like ceramics (Weber *et al.*, 1984), steel (Moriwaki and Shamoto, 1991), and glass (Moriwaki *et al.*, 1992). Traditionally, hard and brittle materials and iron-based alloys were not

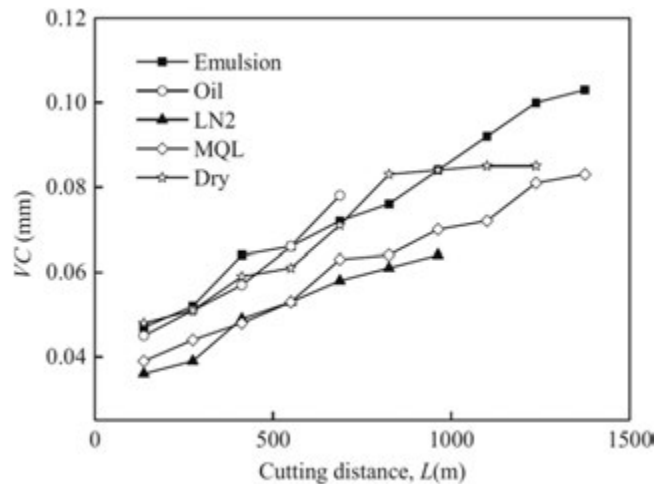


Fig. 9 Flank wear variations with cutting lengths under different cooling and lubrications conditions. Reproduced from Duan, C., Sun, W., Che, M., Yin, W., 2019. Effects of cooling and lubrication conditions on tool wear in turning of Al/SiCp composite. *The International Journal of Advanced Manufacturing Technology* 103 (1–4), 1467–1479.

machined cost effectively with conventional machining technologies. Through the induction of low-amplitude and high-frequency vibration at the cutting edge, these materials can be machined successfully with better surface finishing, improved dimensional accuracy, lower cutting force, prolonged tool life, and increased in productivity. Coupled with the right machining parameters, VAM has been proven reliable to produce crack-free functional surfaces on hard and brittle materials known as ductile-mode machining (Pei and Ferreira, 1998) by facilitating material removal at a special range of undeformed chip thickness. Also, diamond tools that were not previously used in machining iron-based alloys due to the vulnerability of diamonds with the presence of iron under elevated temperatures and pressures has since been successfully revolutionized by using VAM. Through periodical displacement of the cutting tools, heat is unable to build up continuously on the affected zones to reach the necessary temperatures for the onset of graphitization.

Such capable VAM systems are divided based on the number of cutting axis: (1) 1-dimensional; and (2) 2-dimensional where either a linear reciprocating motion or a repetitive bi-axial motion in ellipse are involved. Fig. 10 depicts a 1-D VAM system that typically consists an ultrasonic transducer, sonotrode, and cutting tool mounted on a base plate. According to Brehl and Dow (2008), chips are produced by the cutting tool that is periodically displaced from the workpiece when the linear vibrating frequency is superimposed with the upfeed velocity of workpiece as shown in Fig. 10. On the other hand, a 2-D VAM uses a more complex system based mainly on a 4-piezoelectric actuators control, where each pair governs motions in the vertical and horizontal axes respectively as shown in Fig. 11. Sinusoidal voltage is separately applied to the upper-lower pair and the front-back pair to generate mutually exclusive vibrations in the cutting axis and the axis perpendicular to the cutting axis (Shamoto et al., 2002). With proper regulation of the bi-axial resonance, useful elliptical vibration is generated, and material removal is carried out by diamond tools at the tip of the module. As the tools vibrate elliptically along the main cutting direction, chips are intermittently formed when the tools are brought towards the workpiece while the newly formed chips are seemingly extracted when the tools are brought away from the workpiece. This process as shown in Fig. 11 is cyclically repeated throughout the process. Such cutting action is believed to improve tribological properties, which are beneficial to improve tool wear and surface finish (Xing et al., 2013).

To demonstrate the effectiveness of 1-D VAM in reducing cutting forces, Fig. 12 shows force distributions when Al/SiCp 25 wt% is subjected to turning with PCD tools under vibration-assisted mode and conventional turning (CT) without vibration-assisted as reported by Bai et al. (2019). Continuous material removal was performed without vibration-assisted for a duration of 40 s, which started from preliminary tool engagement at 20-s to 60-s. Then the mode of machining was switched to the vibration-assisted from the 60-sec mark, lasted for another 40 s before disengaging the cutting tool from the workpiece. By introducing ultrasonic vibrations to conventional machining on the same setup while keeping the rest of cutting conditions and parameters entirely constant, the cutting force produced is found to reduce drastically by an approximation of 58%. Reduction in cutting force is of great practical importance since it is a principal component in the functions of cutting energy and thus a reduction in cutting force also implies a corresponding reduction in cutting energy by scale. Aside from primary cutting force, such linear reciprocating motion also led to reductions in feed and thrust force in smaller scales that are positive indicators of a more sustainable process in general.

On top of cutting force, the advantages of VAM can also be observed from the type of chips produced. Fig. 13 illustrates the chips produced by VAM and CT under the same machining conditions in Bai et al. (2019). With vibration-assisted, CT produces 'short C-type' chips that are highly fragmented compare to the long, continuous 'spring-type' chips produced by VAM. The former presents saw-tooth like features on the free surface and multiple fractures on the back surface, which indicate adiabatic shearing

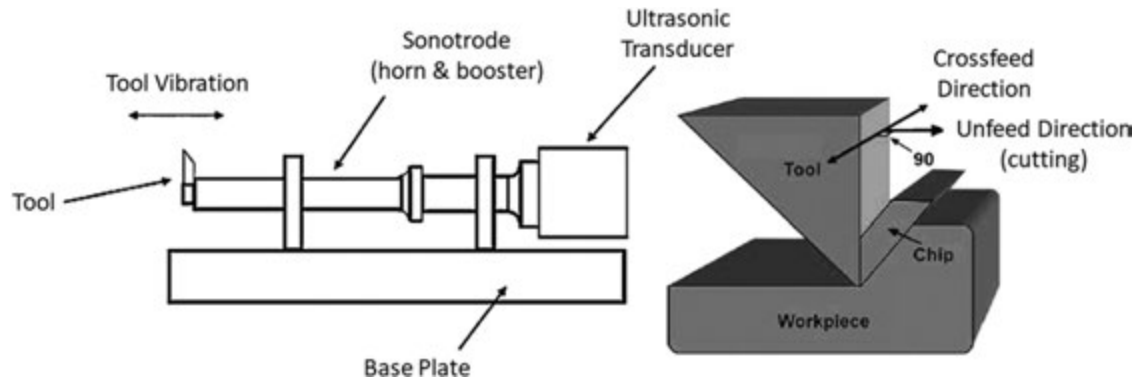


Fig. 10 1-D vibration-assisted machining system and cutting mechanism. Reproduced from Brehl, D.E., Dow, T.A., 2008. Review of vibration-assisted machining. *Precision Engineering* 32, 153–172

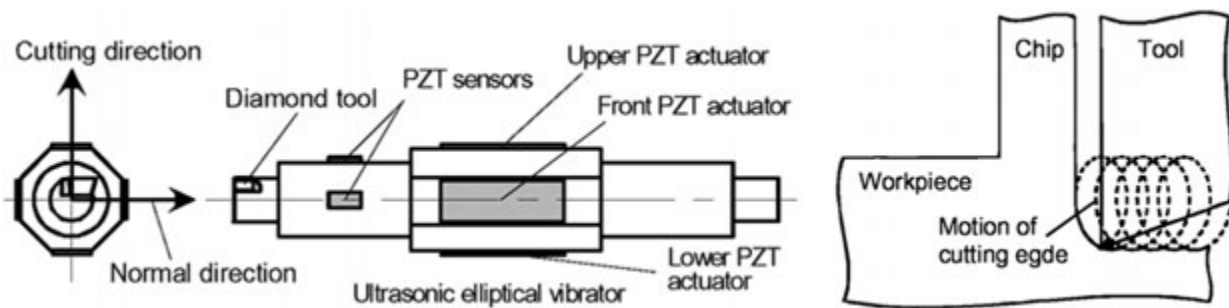


Fig. 11 2-D vibration-assisted machining system and elliptical cutting mechanism. Reproduced from Shamoto, E., Suzuki, N., Moriwaki, T., Naoi, Y., 2002. Development of ultrasonic elliptical vibration controller for elliptical vibration cutting. *CIRP Annals* 51 (1), 327–330.

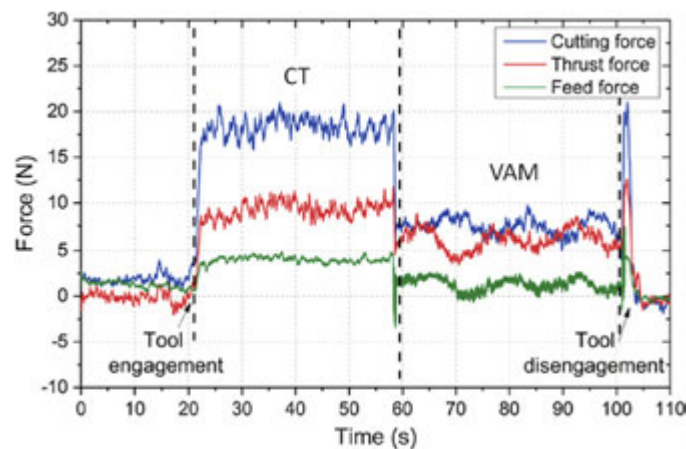


Fig. 12 Drastic reductions in cutting force with vibration-assisted machining. Reproduced from Bai, W., Roy, A., Sun, R., Silberschmidt, V.V., 2019. Enhanced machinability of SiC-reinforced metal-matrix composite with hybrid turning. *Journal of Materials Processing Technology* 268, 149–161.

and random segmentation during chip formation. In contrast, the latter has a continuous, uniform lamella structures on the free surface with little or no fractures on the back surface which in turn, implies a stable history of plastic deformation. The findings are largely due to the tendency of reinforced particles in MMCs to accumulate in the primary deformation zone during chip formation in CT. Chips break into fragments randomly when particles accumulation intensifies, leading to the formation of unstable pile-ups. This explains the distinctively different features and morphology in chips produced with VAM as the vibrating motion at designated ultrasonic frequency has the capability to redistribute reinforced particles from the primary deformation zone back to the matrix and avoid random segmentation of chips due to active particles pile-up.

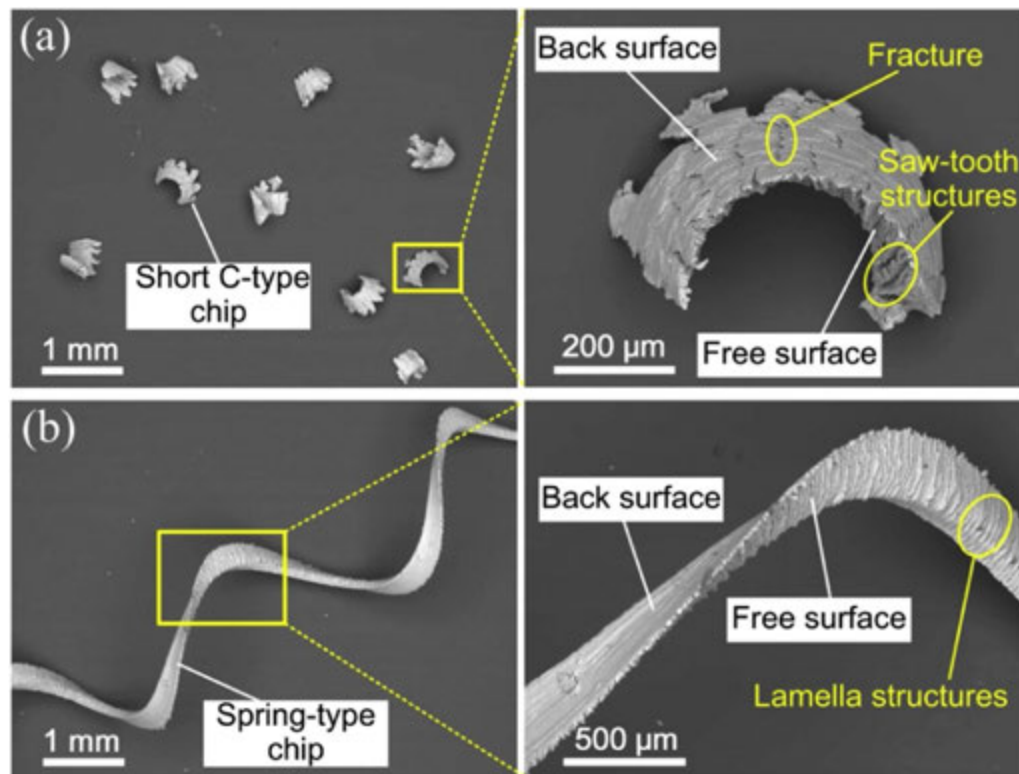


Fig. 13 Different chip types and morphologies produced with (a) conventional turning; and (b) vibration-assisted machining. Reproduced from Bai, W., Roy, A., Sun, R., Silberschmidt, V.V., 2019. Enhanced machinability of SiC-reinforced metal-matrix composite with hybrid turning. *Journal of Materials Processing Technology* 268, 149–161.

From the scale of force reduction to the distinctive chip morphology produced through VAM and CT, the resultant surface topography and quality as shown in Figs. 14 and 15 also differ correspondingly (Bai *et al.*, 2019). Fine, longitudinal grooves are found along the cutting direction on both types of surfaces. These grooves are formed during chip formation when the reinforced particles that accumulate at the primary deformation zone are driven passively by the cutting tool to plow on the machined surface along the tool path. Amid the particle-plowing process under CT, some of the particles tend to unbind and detach from the machined surface that leaves tear-like pitted defects along the longitudinal grooves. Such surface defects are shown in Fig. 14. On the contrary, such pitted defects are not found on machined surfaces produced under vibration-assisted mode as shown in Fig. 15. Particles unbounding is more prone to happen in CT when the particles of different size and at varying depths related to the cutting path are held in chips with uniform thicknesses. This is followed by a secondary detachment from the holding chip leads to the production of highly fragmented chips. These undesirable phenomena can be resolved by introducing ultrasonic vibration motion to machining, which yields long, unfragmented chips with varying thicknesses although the grooves generated on the surface are slightly deeper due to the amplitude of vibration. Improvements in surface roughness up to 15% has been achieved.

Conclusions and Future Outlook

Machining of metal matrix composites (MMCs) is challenging. This article describes the fundamentals behind the challenge, largely attributed to the hard and brittle reinforced particles within the composites that also contribute to the superiority of MMCs in terms of mechanical properties. Since machining relies on the use of solid cutting tools to generate shapes and features, physical interaction between the particles and cutting tools leads to severe abrasive wear, which impairs the effectiveness of chip formation and undermines the overall performance of the machining process. The following conclusions are thus drawn from the present article:

- (1) Polycrystalline diamond (PCD) is the most ideal tool material for MMC machining for its ultimate hardness to resist mechanical abrasion on the surface.
- (2) Combination of uncoated cemented carbide tools for roughing and PCD tools for finishing is the best tooling solution based on pragmatism and cost-effectiveness.
- (3) Emulsions among commercial cutting fluids are best suited for MMC machining to address the equal needs for cooling and lubrication to suppress adhesion.

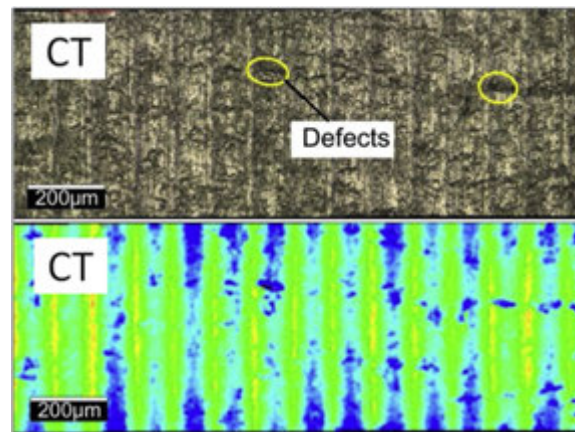


Fig. 14 Defective machined surface produced with conventional turning. Reproduced from Bai, W., Roy, A., Sun, R., Silberschmidt, V.V., 2019. Enhanced machinability of SiC-reinforced metal-matrix composite with hybrid turning. *Journal of Materials Processing Technology* 268, 149–161.

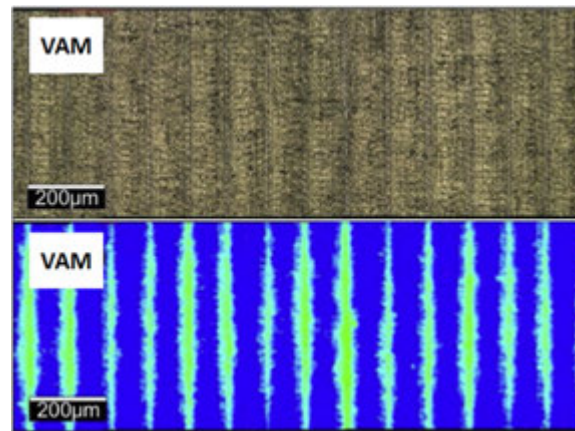


Fig. 15 Machined surface with improved finishing with vibration-assisted machining. Reproduced from Bai, W., Roy, A., Sun, R., Silberschmidt, V.V., 2019. Enhanced machinability of SiC-reinforced metal-matrix composite with hybrid turning. *Journal of Materials Processing Technology* 268, 149–161.

- (4) Supply cutting fluids in minimum quantity with the use of pressurized gas assures efficient delivery through narrow gaps on to the rake and flank faces.
- (5) Vibration-assisted machining (VAM) of MMCs prolongs tool life by disrupting the wear mechanism through periodic tool separation from workpiece.
- (6) VAM that separates cutting tools from workpiece increases cutting fluids accessibility to tool faces, leading to improved tool wear and machining performance.

Based on these findings, the most direct approach to improve the quality and performance in machining MMC is by reducing tool wear and diminishing its impact. Both of which can be readily benefited from robust tool materials, effective cutting fluids application and reduced exposure to harmful abrasion. The future direction of MMC machining research should thus be converging towards the above-stated conclusions.

References

- Bai, W., Roy, A., Sun, R., Silberschmidt, V.V., 2019. Enhanced machinability of SiC-reinforced metal-matrix composite with hybrid turning. *Journal of Materials Processing Technology* 268, 149–161.
- Barnes, S., Pashby, I.R., 1995. Machining of aluminium based metal matrix composites. *Applied Composite Materials* 2, 31–42.
- Brehl, D.E., Dow, T.A., 2008. Review of vibration-assisted machining. *Precision Engineering* 32, 153–172.
- Chou, Y.K., Liu, J., 2005. CVD diamond tool performance in metal matrix composites machining. *Surface Coating Technology* 200 (5–6), 1872–1878.
- Duan, C., Sun, W., Che, M., Yin, W., 2019. Effects of cooling and lubrication conditions on tool wear in turning of Al/SiCp composite. *The International Journal of Advanced Manufacturing Technology* 103 (1–4), 1467–1479.

- El-Gallab, M., Sklad, M., 1998. Machining of Al/SiC particulate metal matrix composites Part II: Workpiece surface integrity. *Journal of Materials Processing Technology* 83, 277–385.
- Everett, R.K., Arsenault, R.J., 1991. *Metal Matrix Composites: Processing and Interfaces*. San Diego: Academic Press.
- Fiytpatrick, M., Smith, K., 2019. *Machining and CNC Technology*, fourth ed. New York: McGraw-Hill Education.
- Gergman, F., Jacobson, S., 1994. Tool wear mechanisms in intermittent cutting of metal matrix composites. *Wear* 179, 89–93.
- Ge, Y.F., Xu, J.H., Yang, H., Luo, S.B., Fu, Y.C., 2008. Workpiece surface quality when ultra-precision turning of SiCp/Al composites. *Journal of Materials Processing Technology* 203 (1–3), 166–175.
- Groover, M.P., 2017. *Groover's Principles of Modern Manufacturing: Materials, Processes, and Systems*, Global edition Asia: John Wiley & Sons Inc.
- Hung, N.P., Boey, F.Y.C., Khor, K.A., Oh, C.A., Lee, H.F., 1995. Machinability of cast and powder-formed aluminum alloys reinforced with SiC particles. *Journal of Materials Processing Technology* 48, 291–297.
- Joshi, S., Ramakrishnan, N., Ramakrishnan, P., 1999. Analysis of chip breaking during orthogonal machining of Al/SiC_p composites. *Journal of Materials Processing Technology* 110, 152–159.
- Kainer, K.U., 2006. *Metal Matrix Composites, Custom-Made Materials for Automotive and Aerospace Engineering*. Weinham: Wiley-VCH.
- Kannan, S., Kishawy, H.A., 2006. Surface characteristics of machined aluminium metal matrix composites. *International Journal of Machine Tools & Manufacture* 46, 2017–2025.
- Klein, C., 2007. *Minerals and Rocks: Exercises in Crystal and Mineral Chemistry, Crystallography, X-ray Powder Diffraction, Mineral and Rock Identification, and Ore Mineralogy*, third ed. Wiley.
- Kremer, A., Devillez, A., Dominiak, S., Dudzinski, D., El-Mansori, M., 2008. Machinability of Al/SiC particulate metal matrix composites under dry conditions with CVD diamond-coated carbide tools. *Machining Science and Technology* 12 (2), 213–233.
- Lane, C., 1992. Machinability of aluminium composites as a function of matrix alloy and heat treatment. *Proceedings of the Machining of Composite Materials Symposium, ASM Material Week*. Chicago, Illinois: ASM.
- Li, X., Seah, W.K.H., 2001. Tool wear acceleration in relation to workpiece reinforcement percentage in cutting of metal matrix composites. *Wear* 247, 161–171.
- Moriwaki, T., Shamoto, E., 1991. Ultraprecision turning of stainless steel by applying vibration. *Annals of the CIRP* 40 (1), 559–562.
- Moriwaki, T., Shamoto, E., Inoue, K., 1992. Ultraprecision ductile cutting of glass by applying ultrasonic vibration. *Annals of the CIRP* 41 (1), 141–144.
- Muthukrishnan, N., Davim, J.P., 2009. Optimization of machining parameters of Al/SiC-MMC with ANOVA and ANN analysis. *Journal of Materials Processing Technology* 209 (1), 225–232.
- Oya, A., Otani, S., 1979. Catalytic graphitization of carbons by various metals. *Carbon* 17 (2), 131–137.
- Pei, Z.J., Ferreira, P.M., 1998. Modeling of ductile-mode material removal in rotary ultrasonic machining. *International Journal of Machine Tools and Manufacture* 38 (10–11), 1399–1418.
- Pramanik, A., Zhang, L.C., Arsecularatne, J.A., 2006. Micro-indentation of metal matrix composites – An FEM analysis. In: *Proceedings of the Eight Asia-Pacific Symposium on Engineering Plasticity and its Applications*, Nagoya, Japan.
- Pramanik, A., Zhang, L.C., Arsecularatne, J.A., 2007. An FEM investigation into the behavior of metal matrix composites: Tool-particle interaction during orthogonal cutting. *International Journal of Machine Tools & Manufacture* 47, 1497–1506.
- Quan, Y., Zhou, Z., 2000. Tool wear and its mechanism for cutting SiC particle-reinforced aluminium matrix composites. *Journal of Materials Processing Technology* 100 (1–3), 194–199.
- Shamoto, E., Suzuki, N., Moriwaki, T., Naoi, Y., 2002. Development of ultrasonic elliptical vibration controller for elliptical vibration cutting. *CIRP Annals* 51 (1), 327–330.
- Shokrani, A., Dhokia, V., Munoz-Escalona, P., Newman, S.T., 2012. State-of-the-art cryogenic machining and processing. *International Journal of Computer Integrated Manufacturing* 26 (7), 616–648.
- Taya, M., Arsenault, R.J., 1989. *Metal Matrix Composites: Thermomechanical Behavior*. England: Pergamon Press.
- Teti, R., 2002. Machining of composite materials. *CIRP Annals* 51 (2), 611–634.
- Tomac, N., Tonnessen, K., 1992. Machinability of particulate aluminum matrix composites. *Annals of the CIRP* 41 (1), 55–58.
- Wang, Y.J., Zhou, M., Huang, S.N., Zhang, Y.J., 2010. Tool wear in high speed milling of SiC_p/Al2024 metal matrix composites. *Applied Mechanics and Materials* 33, 200–203.
- Weber, H., Herberger, J., Pilz, R., 1984. Turning of machinable glass ceramics with an ultrasonically vibrated tool. *Annals of the CIRP* 33 (1), 153–172.
- Weinert, F., 1993. A consideration of tool wear mechanism when machining metal matrix composites (MMC). *Annals of the CIRP* 42 (1), 95–98.
- Xing, D., Zhang, J., Shen, X., Zhao, Y., Wang, T., 2013. Tribological properties of ultrasonic vibration assisted milling aluminium alloy surfaces. *Procedia CIRP* 6, 539–544.

Application of Metal Matrix Composites in Engineering Sectors

Dipen K Rajak, Sandip Institute of Technology and Research Centre, Nashik, Maharashtra, India

Pradeep L Menezes, University of Nevada, Reno, NV, United States

© 2021 Elsevier Inc. All rights reserved.

Introduction

The demand for technological advancement is gradually increasing for the ease of potential applications in various sectors, which comprise of science, engineering, and biomedical industries. An engineering sector can be broadly classified into manufacturing, automobile, aerospace, marine, and defense. The composite is the combination of different materials that have dissimilar physical and chemical structures. These materials which are combined to form the composite are known as the constituent materials. The constituent materials can be metals, non-metals, organics, or in-organic materials. The composite materials are categorized into three types based on matrix materials, which are polymer matrix composites (PMCs), ceramic matrix composites (CMCs), and metal matrix composites (MMCs). The composite material, which consists of a metal matrix combining with another hard reinforcement, is known as MMCs (Haghshenas, 2016; Trinh and Sastry, 2016; Vijaya Ramnath and Elanchezhian, 2013; Moonaa *et al.*, 2018). Nowadays, various types of materials are in the developing phase to incline with the properties and applications in demand. The researchers are gaining tremendous interest in the composite materials amongst the other materials. The reasons behind the development of the composite materials are due to their excellent mechanical, physical, chemical, and thermal properties, which develop due to the combinations of different materials (Haghshenas, 2016; Mavhungu, 2017; Dasgupta, 2012; Stojanovic and Ivanovic, 2015). The composite material consists of metal as a matrix material, and a doping material, i.e., reinforcement, for improving its properties. The MMCs utilize the matrix material and the reinforcements for obtaining high strength, stiffness, ductility, wear resistance, creep resistance, fatigue resistance, toughness, and corrosion resistance (Haghshenas, 2016; Dasgupta, 2012; Hunt and Miracle, 2001; Prasad and Asthana, 2001; Pai *et al.*, 2004; Allison and Cole, 1993). The cost, performance, and properties of the MMCs depend on the production technique and the type or volume fraction of the material used for reinforcement (ceramic). Matrix materials in the MMCs are either pure metals or alloys. The different types of matrix materials usually used in the MMCs are stated as follows (Trinh and Sastry, 2016; Pai *et al.*, 2004; Allison and Cole, 1993; Kevorkijan, 1999; Rohatgi *et al.*, 2006; Bechmann *et al.*, 2007; Miracle, 2005; Rajak *et al.*, 2020; Rajak *et al.*, 2019), (1) aluminum, (2) copper, (3) magnesium, (4) titanium, (5) nickel and (6) iron. The reinforcement material is the material that improves the properties of the MMCs, usually the strength and/or stiffness. The most frequently used reinforcement materials are ceramics (nitrides, carbides, oxides, etc.). The examples of reinforcements for some MMCs are SiC, Al₂O₃, TiB₂, B₄C, and graphite. The MMCs are classified according to the type and geometric characteristics of the reinforcement materials as shown in Fig. 1.

The selection of suitable reinforcement material depends upon the type of applications, compatibility, and interfacial resistance between the matrix and reinforcement material (Trinh and Sastry, 2016). Continuous reinforcement results in the improvement of properties like wear resistance, thermal expansion coefficient, and thermal conductivity. Discontinuous reinforcement has positive effects on hardness, fatigue resistance, wear-resistance, and dimensional stability. It also results in better stiffness but at the cost of low ductility and fracture toughness (Trinh and Sastry, 2016; Rajak *et al.*, 2019; Elmarakbi, 2014; Miyamoto, 2013; Rashad *et al.*, 2015; Mustafa and Abdulgadir, 2017; Holley, 2013; Peng, 2005; Guo and Derby, 1995; Hayat *et al.*, 2019; Singerman and Jeffrey, 1998; Welsch *et al.*, 1993; Leyens and Peters, 2003). Fig. 2 shows the schematic diagram of the structure of different kinds of MMCs with respect to reinforcement materials.

Properties of MMCs

The MMCs possess a variety of applications, due to their typical properties viz. (1) elevated temperature capabilities, (2) higher radiation resistance, (3) higher transverse strength and stiffness, (4) least moisture absorption, (5) high thermal and electrical conductivity, (6) higher Young's modulus, (7) higher fatigue strength (at elevated temperatures), (8) low density, and (9) high wear and corrosion resistance (Haghshenas, 2016). Along with these advantages in properties, the few drawbacks are (1) expensive production systems; (2) technology is still under developing stage as compared to others, (3) complexity in the manufacturing (especially in case of the long fiber MMCs).

Classification of MMCs

The main categories were explained in the section above. The following are possible sub-combinations of reinforcement material with respect to matrix material:

- Aluminum-based MMCs
 - Long fiber: alumina, silicon carbide, boron, graphite
 - Short fiber: alumina, alumina-silicon
 - Whiskers: silicon carbide
 - Particle: silicon carbide, boron carbide

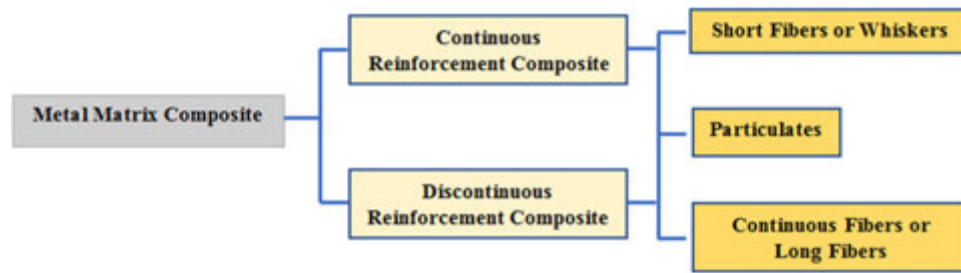


Fig. 1 Reinforcement based MMCs. Reproduced from Trinh, S.N., Sastry, S., 2016. Processing and properties of metal matrix composites. Mechanical Engineering and Materials Science Independent Study, 10.



Fig. 2 Structure of MMCs based on reinforcement. Reproduced from Trinh, S.N., Sastry, S., 2016. Processing and properties of metal matrix composites. Mechanical Engineering and Materials Science Independent Study, 10.

- Magnesium-based MMCs
 - Long fiber: alumina, graphite
 - Whiskers: silicon carbide
 - Particle: silicon carbide, boron carbide
- Titanium-based MMCs
 - Long fiber: silicon carbide
 - Particle: titanium carbide
- Copper-based MMCs
 - Long fiber: silicon carbide, graphite
 - Particle: titanium carbide, silicon carbide, boron carbide
 - Filament: niobium-titanium
- Super alloys based MMCs
 - Filament: tungsten

Aluminum-Metal Matrix Composites (AMMCs)

The aluminum alloys have excellent thermal conductivity and lower weight, because of which they have numerous applications in the field of automobile, aerospace, and mineral processing (Dasgupta, 2012; Leyens and Peters, 2003; Li *et al.*, 2013; Air Force Technology, 1997; Specialty Materials, Inc.; Liu *et al.*, 2006). It has been discovered that the use of lightweight material with suitable strength has become a priority for researchers (Trinh and Sastry, 2016; Moonaa *et al.*, 2018; Singerman *et al.*, 1996; Connell, 1973; Anderson, 1998; Salvo and Mangalaraja, 2018; Franczak and Karwan-Baczewska, 2017; Rao, 2017; Rajkovic *et al.*, 2010; Hong, 2011; Shehata, 2009; Moghadam, 2015; Lu, 2004; Duarte and Ferreira, 2016). Modern cars are equipped with large screens, electronic amenities, multimedia gadgets etc (Vijaya Ramnath and Elanchezhian, 2013; Leyens and Peters, 2003). This also results in additional weight to the vehicle, which results in increased fuel consumption and environmental pollution. For providing the counterweight to the excess weight added, the aluminum-based MMCs were targeted. Fig. 3 shows the micro-structure of aluminum-based MMCs, with SiC particle distributions in the matrix.

The need for obtaining different MMCs based on Al is gaining significant interest and attention from the researchers. These AMMCs contain a variety of improved qualities. These include better strength to weight ratio, higher strength, high elastic modulus, good ductility, excellent resistance to wear, lower coefficient of thermal expansion, excellent corrosion resistance, high temperature creep resistance and fatigue strength. The reinforcements and the processing methods are majorly responsible for the improved properties in AMMCs (Vijaya Ramnath and Elanchezhian, 2013). The recently used reinforcement materials are mostly ceramics (Al_2O_3 , SiC, MgO and B_4C). The properties of these reinforcement materials like refractoriness, high compressive

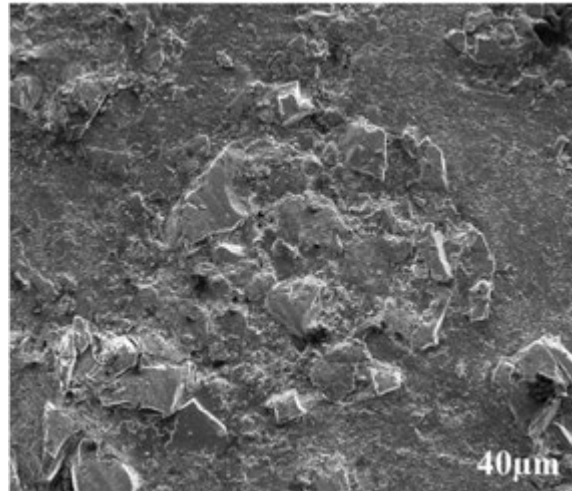


Fig. 3 SiC-particle reinforced aluminum-matrix composite material (D.K. Rajak ©).

Table 1 Properties of Aluminum-based MMCs

Properties	Matrix Metal (1)*	Particulate MMCs (2)*	Fiber MMCs (3)*
Strength (MPa) (axial)	290	290–489	620–1240
Stiffness (GPa) (axial)	70	290–480	130–450
Transverse strength (MPa)	290	290–140	30–170
Transverse stiffness (GPa)	70	80–140	34–173
Plane strain fracture toughness (MPa-m)	18–35	12–35	–

Where, (1)* 6061-aluminum, (2)* 6061-aluminum reinforced with 0%–40% of SiC particulate by volume, (3)* 6061-aluminum 50% reinforced with fibers of SiC, graphite, boron, and alumina by volume.

Note: Trinh, S.N., Sastry, S., 2016. Processing and properties of metal matrix composites. Mechanical Engineering and Materials Science Independent Study, 10.

strength, hardness, wear resistance, etc., make them superior to the other reinforcement materials (Moonaa *et al.*, 2018; Dasgupta, 2012; Tjong, 2013; Geim and Novoselov, 2007; Ramkumar, 2018; Mikula *et al.*, 2015; Rawal, 2001; Collins and Mikko, 2000).

Properties of AMMCs

- High strength
- High stiffness
- Reduced density (weight)
- Improved creep resistance at high temperatures
- Moderate coefficient of thermal expansion
- Improved electrical conductivity
- Improved abrasion and wear resistance
- Controlled weight
- Moderate toughness
- Moderate ductility (depends on reinforcement type)

Some essential mechanical properties of the matrix material, particle, and fiber in a comparative way are shown in Table 1. Following categories of AMMCs are:

- Silicon carbide reinforced
- Aluminum oxide reinforced
- Boron carbide reinforced
- Fiber reinforced
- Zircon reinforced
- Fly ash reinforced

Applications of AMMCs

More than 50% of the production of MMCs has applications in the automotive industry. The MMCs are used in modern cars, due to their expensive processing techniques. The applications of AMMCs are demonstrated in brief in the following section (Hunt and Miracle, 2001; Miyamoto, 2013). **Table 2** depicts the applications of aluminum-based MMCs with respect to the manufacturer, composite material, and components in a comparative pattern (Stojanovic and Ivanovic, 2015).

Engine pistons

Engine pistons work under extremely harsh mechanical, dynamical, and thermal conditions. The piston undergoes the cyclic mechanical loading with a frequency of around 100 Hz (Stojanovic and Ivanovic, 2015). Thus, the provision for fatigue strength is primarily important. During the expansion periods, the piston must provide intimate contact with the cylinder under maximal pressures to avoid the pressure drop. The pressure drops lead to astonishing power loss. It is also requisite for the piston to operate at a temperature of around 3000°C (Stojanovic and Ivanovic, 2015), which is generated in the engine while working for a long time. This temperature variation causes thermal impacts, which can be avoided by providing high thermal conductivity. **Fig. 4** shows the actual sectional view of a piston produced with AMMCs.

In 1983, a reputed Japanese automobile manufacturer named Toyota car manufacturer started the production of pistons for diesel engines. The material used for the production was AMMC, which proved to be a breakthrough in applications (Hunt and Miracle, 2001; Miyamoto, 2013). Those composites were produced by the squeeze casting technique (SCT), which resulted in large

Table 2 Some of the Al matrix composite applications along with the manufacturers

<i>Manufacturer</i>	<i>Composite</i>	<i>Component</i>
Duralcan, Martin marietta, Lanxide	Al/SiCp	Pistons
Duralcan, Lanxide	Al/SiCp	Calipers, Brake rotors, Liners
GKN, Duralcan	Al/SiCp	Propeller shaft
Nissan	Al/SiCw	Connecting rod
Dow chemical	Mg/SiCp	Pulleys, Sprockets
Toyota	Al/Al ₂ O ₃	Piston rings, Al/Boriaw and saffil
Dupont, Chrysler	Al/Al ₂ O ₃	Connecting rods
Hitachi	Cu/Graphite	Current collectors
Martin Marietta	Al/TiCp	Pistons, Connecting rods
Honda	Al/Al ₂ O ₃ – Cf	Engine blocks
Lotus Elise, Volkswagen	Al/SiCp	Brake rotors
Chrysler	Al/SiCp	Brake rotors
GM	Al/SiCp	Engine cradle, rear brake drum for EV-1, driveshaft
MC – 21, Dia-Compe, Manitou	Al/SiCp	Disk brake rotors, bicycle fork brace
3M	Al/Nextelf	Missile fins, aircraft electrical AC door
Kobenhavn, Knorr-Bremse	Sic/Al	Brake disk on ICE bogies
Alcoa Innometalx	Al/SiCp	Multichip electronic module
Lanxide	Al/SiCp	PCB heat sinks
Cercast	Al/Graphite foam	Electronics packages
Textron Specialty Materials	Al/B	PCB heat sinks

Note: Mavhungu, S.T., 2017. Procedia Manufacturing 7, 178–182.



Fig. 4 Pistons made of AMMCs. Reproduced from Stojanovic, B., Ivanovic, L., 2015. Application of aluminum hybrid composites in automotive industry. Tehnicki Vjesnik 22 (1), 247–251.

scale production of over 1,00,000 items per mount. This production rate resulted in excellent quality at satisfactory costs. The ceramic reinforcements in the MMCs used for producing the pistons had higher wear resistance as compared to the matrix material (Stojanovic and Ivanovic, 2015). Simultaneously, pistons possessing lower values of thermal expansion coefficient result in the provision of narrow tolerances. The requirement of narrow tolerances provides an increase in maximum pressures allowed and thus improved thermal properties. Besides that, the method of piston fabrication and the casting of MMCs are quite similar (Hunt and Miracle, 2001). The price of aluminum material is high, but the cost of pistons is comparatively lower than the pistons produced using traditional materials. Silicon carbide (SiC) is usually used as the reinforcement material in the MMCs used in race cars. The Asian and western European car producers heavily use pistons made of MMCs (Stojanovic and Ivanovic, 2015).

Engine cylinders

Substantial use of aluminum alloys for the production of the engine block led AMMC to find its application in manufacturing engine cylinders. In 1990, mass production of the cylinder barrel made of AMMC had emerged. In the beginning, AMMC was used in 2.3 L of Honda Prelude engine, which was made of aluminum matrix hybrid composite material with reinforcement of carbon and Al_2O_3 (Hunt and Miracle, 2001). The production process used for cylinder barrel was squeeze casting at moderate pressure. Fig. 5 shows the sectional view of the engine block cylinder barrel (EBCB) of Honda Prelude produced with AMMCs.

AMMC shows higher resistance to wear than that of cast iron (Stojanovic and Ivanovic, 2015). By application of AMMCs, the overall engine block weight is reduced by 20%. Also, the increase in work volume was achieved without redesigning due to the thickness of the cylinder barrel, which was lesser than the one made from cast iron. The engines with cylinder barrel made of AMMCs are efficiently deployed in Honda S2000 sports cars, Acura NSX cars, and Porsche Boxster Motors. The engines of Toyota Celica 2000 series cars also consist of cylinder barrels made of AMMCs (Stojanovic and Ivanovic, 2015). AMMC made cylinder barrels are used in high-performance Honda Motorbikes.

Engine pushrods

Fiber reinforced AMMCs are used for the production of valve pushrods in engines. The matrix used is an aluminum alloy, while fibers of Al_2O_3 are used as the reinforcing material. 3M Corporation initially started the production of parts made of AMMCs. AMMC made pushrods showed 25% higher stiffness and twice the shock absorption capacity than the parts made of standard steel. Also, the exploitation period of AMMC made pushrods is also exceptionally higher than the ones produced with steel. The engine pushrods produced with AMMCs are shown in Fig. 6. Rotations per minute (rpm) can be increased to 200–400 without the addition of dynamic loads, due to lesser density and weight.

Engine connecting rod

By producing the connecting rod (see Fig. 7) with AMMCs, the mass reduction of 57% can be achieved as compared to the steel ones. The mass reduction of the piston or connecting rod results in the reduction of vibration during operation. This results in many positive effects, such as lessen the load on the crankshaft and bearings, energy losses due to friction and fuel consumption. It is discovered that the decrease in 1 kg of mass in crankshaft results in a reduction of 7 kg of mass in balancing counterweight. The connecting rods produced with the reinforcement of SiC and Al_2O_3 are deployed by Nissan and Dupont/Chrysler, respectively (Miracle, 2005). The implementation of AMMC for the production of the connecting rods results in lesser fuel consumption with the improvement of engine power, but, simultaneously, there is an increase in the total production cost (Prasad and Asthana, 2001). Furthermore, the researchers of MMCs are making some rapid approaches for producing different materials used in making the engine connecting rods (Kevorkian, 1999), and the research in this field is still in progress.

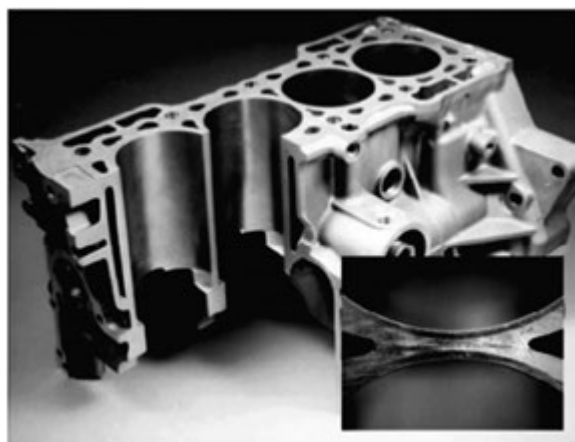


Fig. 5 Engine of Honda Prelude with cylinder barrel made of AMCs. Reproduced from Stojanovic, B., Ivanovic, L., 2015. Application of aluminum hybrid composites in automotive industry. *Tehnicki Vjesnik* 22 (1), 247–251.

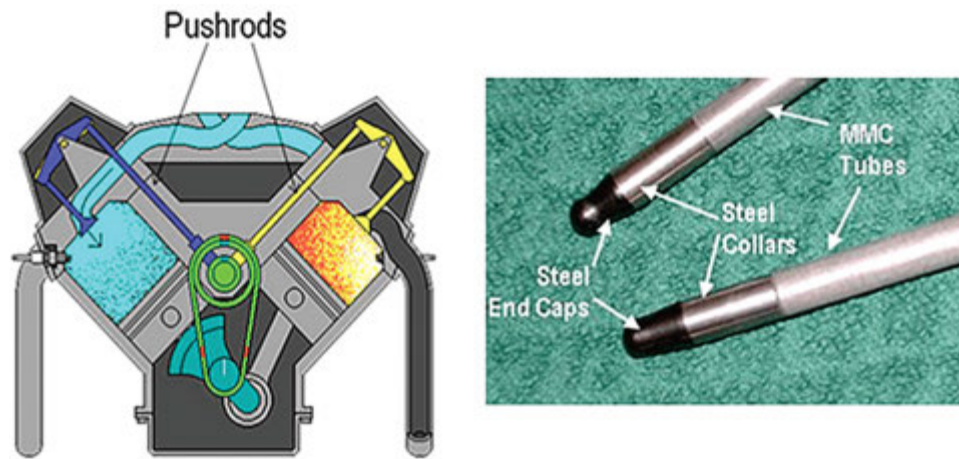


Fig. 6 Engine pushrods made of AMMCs. Reproduced from Stojanovic, B., Ivanovic, L., 2015. Application of aluminum hybrid composites in automotive industry. *Tehnicki Vjesnik* 22 (1), 247–251.



Fig. 7 Piston connecting rod made of AMMCs. Reproduced from Stojanovic, B., Ivanovic, L., 2015. Application of aluminum hybrid composites in automotive industry. *Tehnicki Vjesnik* 22 (1), 247–251.

Brake systems

Disks and drums in a braking system of vehicle are being produced by AMMCs due to their beneficial properties like high wear resistance and high thermal conductivity. **Fig. 8** shows the components of the brake system which use the AMMCs as the parent material. There is a significant reduction in inertia forces, net weight, and fuel consumption, due to a decrease in the weight of material deployed. Brake disks and drums are manufactured by Al-Mg and Al-Si alloy materials reinforced with ceramic materials (such as SiC, Al_2O_3). With the volumetric share of 20% reinforcing materials in the AMMCs, the production processes use unique casting methods. A large number of producers are now using AMMCs for the production of brake systems in the automotive industry.

At Lotus Elise (1996–1998), and Plymouth Prowler uses a rear set of brakes system produced with AMMCs. Discontinuous reinforced AMMCs is used in disk brakes of Volkswagen Lupo 3L and Audi A2. Hybrid and electrical vehicles, such as Toyota RAV4, Ford Prodigy, and General Motors Precept are also equipped by the brake systems produced with AMMCs (Hunt and Miracle, 2001). The high-speed train in Germany, InterCity Express (ICE), also uses the discontinuous reinforced AMMC brake disks (Hunt and Miracle, 2001). Braking pads produced with AMMCs are also deployed in Porsche 911 series. All of these composites consist of ceramic reinforcements.

Propeller shaft

For the manufacturing of propeller shafts, AMMCs are deployed due to their high specific stiffness. The major drawback of the new propeller shaft is its critical rotational speed, which makes it dynamically unstable. The shaft length, its internal and external diameter, and the specific stiffness decide the critical rotational speed of the shaft (Stojanovic and Ivanovic, 2015). Deployment of propeller shaft with AMMCs provides flexibility over designs, for example, increasing the shaft length while keeping the diameter constant or decreasing the shaft diameter while keeping the length constant. Structural weight reductions are obtained at such dimensions, which provide beneficial possibilities for alternative design solutions. Reinforcement of ceramic material, Al_2O_3 , with



Fig. 8 Brake systems made of AMMCs. Reproduced from Stojanovic, B., Ivanovic, L., 2015. Application of aluminum hybrid composites in automotive industry. *Tehnicki Vjesnik* 22 (1), 247–251.



Fig. 9 Propeller shaft of Chevrolet corvette. Reproduced from Stojanovic, B., Ivanovic, L., 2015. Application of aluminum hybrid composites in automotive industry. *Tehnicki Vjesnik* 22 (1), 247–251.

a matrix of Al 6061 is deployed using the stir casting production process. At the beginning of 1997, propeller shafts made of Al_2O_3 -Al 6061 composite were first applied in Chevrolet S-10 and GMC Sonnomo delivery truck. Propeller shafts made from AMMCs were also used in the Chevrolet Corvette and Ford Crown Victoria, which is shown in [Fig. 9](#).

Other applications in automobile

Brake caliper assemblies, turbine blade, gear pairs, turbo-compressors, belt pulleys, valves, pump housings, and supporting parts are also getting manufactured by AMMCs due to their material properties and specific characteristics. Higher wear resistance, lower coefficient of thermal expansion with improved thermal properties are some potential advantages provided by the AMMCs for the production of machine parts. AMMC prices are reducing with the trend of an increasing quantity of produced parts; otherwise, prices are still high ([Stojanovic and Ivanovic, 2015](#)). The AMMCs also have potential applications in the electronic packaging industry, which is represented in [Fig. 10](#).

Magnesium-Metal Matrix Composite (MMC)

MMCs based on magnesium alloys such as Mg-Al are in demand nowadays as it serves the market need of a lightweight, high-performance materials for civic, military, and aerospace applications ([Mustafa and Abdulgadir, 2017](#)). MMCs are also showing conceivable applications in the automotive industry, such as gears, gearbox bearings, disk rotors, piston ring grooves, connecting rods, and shift forks. One of the drawbacks of magnesium-based MMC is higher production costs due to their complex manufacturing processes. Growing demands of high-performance magnesium MMC materials incites researchers to develop a diverse range of reinforcement materials with advanced composite manufacturing techniques. Magnesium-based MMCs, when reinforced with continuous carbon fibers, showed 1000 MPa bending strength with a material density of 1.8 g/cm^3 . The condescending mechanical properties can be retained at elevated temperatures



Fig. 10 Discontinuous reinforced aluminum MMCs for electronic packaging applications. Reproduced from Rawal, S., 2001. JOM 53 (4), 14–17.

Table 3 Comparison of pure Mg and (Mg/0.3 wt% GNPs) composite mechanical properties

Materials	Elastic Modulus (GPa)	0.2% Yield Strength (YS) (MPa)	Ultimate Tensile Strength (MPa)	Strain Failure (%)	Vickers Hardness (HV)
Pure Mg	13.2 ± 0.3	187 ± 4	219 ± 5	3.45 ± 0.5	57.5 ± 2
Mg/0.3 wt% GNPs	14.6 ± 0.2	197 ± 3.1	238 ± 6	3.11 ± 0.4	68.5 ± 2

Note: Rashad, M., Pan, F., Asif, M., 2015. Graphene Materials, 153–190. Mustafa, M., Abdulgadir, D.B., 2017. International Research Journal of Engineering and Technology 4 (4).

in the range of 350–400°C (Rashad *et al.*, 2015). Mg-Al alloys, such as AM60 and AZ91, are currently the most common magnesium alloys used in the automotive industry. Ceramic materials are being widely used as reinforcement material in magnesium matrix composites due to their advancement in properties such as thermal stability, lower material density, high strength, hardness and elastic modulus value (Rashad *et al.*, 2015). When compared to other ceramics, SiC particulates are popular reinforcement employed for MMC material due to its relatively high degree of wettability and stability in magnesium melt (Mustafa and Abdulgadir, 2017).

Properties of Magnesium Based MMCs (Rashad *et al.*, 2015)

- Light weight
- Excellent stiffness to weight ratio
- Low density (2/3 of aluminum)
- Excellent high-temperature mechanical properties
- Good corrosion resistance
- High specific strength
- Improved damping
- Low coefficient of thermal expansion

Tables 3 and 4 represents the comparison of mechanical properties between pure magnesium and its composite at different content and type of reinforcements.

Types of Magnesium Based MMCs

- Silicon carbide reinforced magnesium (SCRM)
- Boron carbide reinforced magnesium (BCRM)
- Fiber reinforced magnesium (FRM)
- CNT reinforced magnesium (CNT-RM)
- Aluminum oxide reinforced magnesium (AORM)
- Titanium carbide reinforced magnesium (TCRM)

Table 4 Properties of magnesium-based MMCs at different content and type of reinforcements

Materials	0.2% Yield Strength (MPa)	Specific Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Specific Ultimate Tensile Strength (MPa)	Ductility (%)
Mg	100	58	258	148	7.7
Mg-2% Cu	281	148	335	177	2.5
Mg-4% Cu	355	170	386	184	1.5
Mg-7% Cu	–	–	433	195	1.0
Mg-2% Ni	337	177	370	194	4.8
Mg-3% Ni	420	203	463	224	1.4
Mg-6% Ni	–	–	313	131	0.7
Mg-2% Ti	163	90	248	127	11.1
Mg-4% Ti	154	81	239	126	9.5
Mg-30% SiC (Particulate)	229	105	258	118	2.0

Note: Trinh, S.N., Sastry, S., 2016. Processing and properties of metal matrix composites. Mechanical Engineering and Materials Science Independent Study, 10.

Applications of Magnesium Based MMCs (Rashad *et al.*, 2015)

- Castings for gearboxes, transmissions, intermediate compressors, auxiliary gearboxes, generators, canopies, and engine components are some of the aerospace applications.
- Due to its light-weight and mechanical properties, it has potential applications in motor racing for reducing vehicle weights.

Titanium-Metal Matrix Composites (TMMCs)

Continuous silicon carbide (SiC) fibers reinforced in titanium metal matrix composite (TMMC) material is leading in aerospace applications in topmost countries, including the UK, USA, France, and China (Peng, 2005). A formidable mixture of stiffness, specific strength, resistance to creep, and fatigue at elevated temperatures is contingent by TMMCs. Advancement in the Ti-based MMC manufacturing techniques has been achieved by several solid-state processing techniques. They are foil fiber foil (FFF) method, matrix coated mono tape (MCM) method and the matrix coated fiber (MCF) method, due to the active behavior of titanium (Holley, 2013). With a very uniform and fine-grained fiber distribution in MCF, the fiber volume fraction of the maximum up to 80% can be achieved (Holley, 2013). Al-reinforced titanium-based MMCs find a wide range of applications in automotive and aerospace industries, the titanium and its alloys are rapidly becoming a part of significant research interest. These materials reveal attractive properties like high strength to weight ratio, excellent biocompatibility with chemical resistance. Such a combination of exceptional properties of these materials makes them an ideal candidate for structural, chemical, petrochemical, marine, and biomedical applications. For the past 30 years, there is a great use of TMCs in aircraft engines and airframe applications, and still being under significant development and evaluation. The main catalytic reason behind its usage for airframe applications is due to its high specific modulus. The introduction of TMCs in high-performance applications has not been straight forward due to its complexities in fabrication, and high material and implementation costs. To increase its usage for industrial applications, consistent efforts on TMCs research were made in the earlier days by the National Aeronautics and Space Administration (NASA). One such example, where six US companies came forward to join forces for the research and development for the implementation of TMCs into large gas turbine engines and form titanium matrix composite turbine engine composite consortium (TMCTECC) program (Hayat *et al.*, 2019). Titanium and Ti alloys are rapidly becoming a part of remarkable research interest for extensive applications in the automotive and aerospace sectors. These materials are light in weight and frequently shown irresistible properties, such as high specific strength, eminent chemical resistance, and exceptional biocompatibility. The combination of these properties makes them a vital candidate for structural, chemical, petrochemical, marine, and biomedical deployments (Welsch *et al.*, 1993; Leyens and Peters, 2003; Li *et al.*, 2013). The Young's modulus, resistance to wear, and heat of titanium materials are subservient to steel and nickel based alloys. TMMCs serve as an alternative to conquer these drawbacks. TMMCs have been under consequential development and evaluation in the past 30 years for deploying in aircraft engines and airframe applications (Liu *et al.*, 2006; Singerman *et al.*, 1996). The advantage of high specific modulus and high specific strength of TMMCs are the main reasons for its deployment in airframes and engine applications. TMMCs based on titanium aluminide that consist of temperature potentiality of reaching to 760°C offers a promising 50% weight reduction as compared to nickel-based super alloys for elevated temperature compressor applications (Liu *et al.*, 2006; Anderson, 1998; Salvo and Mangalaraja, 2018). The initiation of TMMCs into high-performance applications has been complicated due to the complexities in fabrication, high-cost material, and deployment costs. Due to these earlier efforts, the recent advancement and success stories of TMMCs are achievable (Welsch *et al.*, 1993).

Types of Titanium-Based MMCs

Depending on the form of reinforcements, the common TMMCs can be categorized into two groups (Welsch *et al.*, 1993):

- Continuously reinforced TMMCs
- Discontinuously reinforced TMMCs

Properties of Titanium-Based MMCs

Table 5 depicts the comparison of conventional Ti-MMC, Ti-aluminide-MMC, and super-alloys comparatively.

Applications of TMMCs

The schematic representation in the turbojet engine is shown in Fig. 11(a). US famous fighter aircraft F-22 amounts to ~39% titanium and 24% deployment of composites (Air Force Technology, 1997) and development of new generation F-35 fighter planes expecting this amount more likely to be raised. Similarly, the lower drag brace of the landing gear is achieved with SiC fiber reinforced in the TMMCs for Royal Netherlands Air Force F16 (Specialty Materials, Inc.). The actual images of the US Aircraft (F-16, F-22, and F-35) are shown in Fig. 11(b). The TMMC replacement purveys 40% weight reduction in contrast to the original one, which was produced with high-strength steel. Moreover, when compared to steel or aluminum, the metallic composite materials show efficient corrosion resistance and fatigue resistance.

Recently, for the advancement in ultra-fan engine design, the Rolls Royce approaches the testing of a carbon or titanium-based composite fan system. This system includes fan blades made of carbon or titanium with a composite casing, which reduces weight up to 1500 lb per aircraft. This composite fan system of Rolls Royce for new engine designs is shown in Fig. 12(a). This weight reduction is equivalent to the cost of an additional seven passengers. In comparison with the first generation Trent engine (TE), this engine burns 20% less fuel with lesser CO₂ emissions (Welsch *et al.*, 1993). The connecting rods and engine valves made of DRTCs are being deployed by Toyota Motors in their cars. The landing gear of a Royal Netherlands Air Force F-16 is shown in (Fig. 12(b)).

Table 5 Comparison of Ti-MMCs and super-alloys properties

Property	Conventional Ti MMC	Ti Aluminide Ti MMC	Super-alloys
Density (g/cm ³)	4.04	4.18	8.3
0° Stiffness (GPa)	200	242	207
90° Stiffness (GPa)	145	200	207
Maximum Useable Temperature (°C)	538	760	1090
0° CTE (°C ⁻¹ × 10 ⁻⁶)	7.20	7.92	13.0
90° CTE (°C ⁻¹ × 10 ⁻⁶)	8.91	9.18	13.0

Where, 0° = Direction of fiber, 90° = Transverse to direction of fiber, CTE = Coefficient of thermal expansion.

Note: Singerman, S.A., Jeffrey, J.J., 2018. Pratt & Whitney West Palm Beach FL. GE Aircraft Engines.

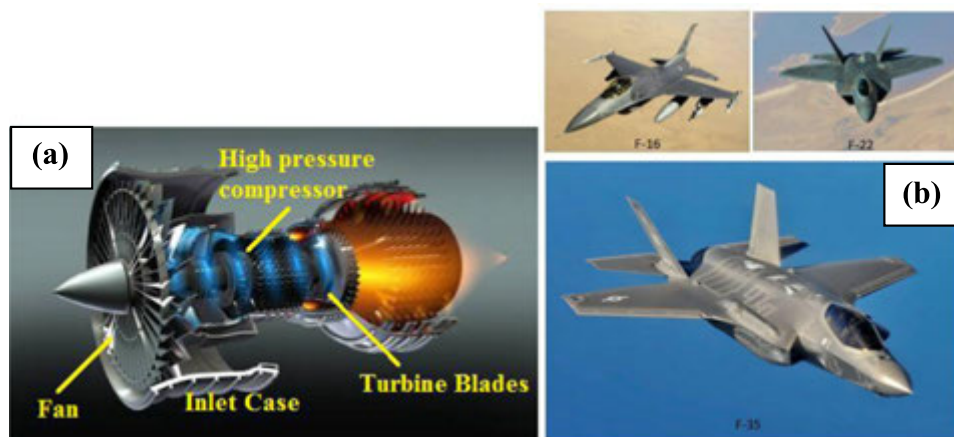


Fig. 11 (a) Potential engine applications and payoffs for TMMCs, (b) Usage of titanium composites in US fighter aircraft. Reproduced from Singerman, S.A., Jeffrey, J.J., 2018. Pratt & Whitney West Palm Beach FL. GE Aircraft Engines. Welsch, G., Boyer, R., Collings, E., 1993. Materials Properties Handbook: Titanium Alloys. ASM International.

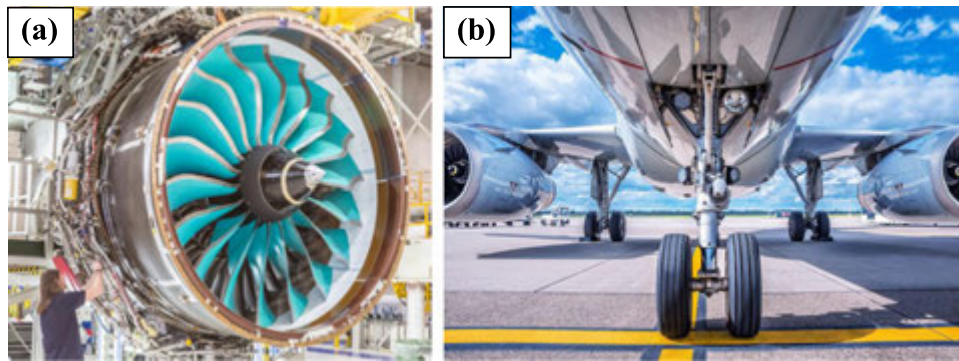


Fig. 12 (a) Rolls Royce composite fan system for new engine designs, (b) TMMC lower drag brace for the landing gear on a Royal Netherlands Air Force F-16. Reproduced from Welsch, G., Boyer, R., Collings, E., 1993. *Materials Properties Handbook: Titanium Alloys*. ASM International.

Copper-Metal Matrix Composites (CMMCs)

Distinctive properties can be achieved, such as high thermal and electrical conductivity, high strength, and excellent thermal resistance to withstand internal stresses when Al_2O_3 particles are disseminated in the copper matrix. The application includes resistance welding electrodes, lead frames, and electrical connectors (Franczak and Karwan-Baczewska, 2017). The materials for electronic packaging and thermal management deployments demand the reconcilable coefficients of thermal expansion (CTE) with those containing semiconductors or ceramic substrates, which shows effectively high thermal conduction and excellent mechanical properties. The combination of significant properties of Cu SiC-MMC materials, such as high thermal conductivity of copper (Cu) and low coefficient of thermal expansion (CTE) of SiC produced to serve as a great solution for thermal management (heat management system) (Rajkovic et al., 2010). Conventional materials such as copper/tungsten (Cu/W), copper/molybdenum (Cu/Mo), copper-Invar-copper (Cu/I/Cu), and copper-molybdenum-copper (Cu/Mo/Cu) alloys possess a low coefficient of thermal expansion (CTE) with high densities and thermal conductivities. Copper-SiC composites provide a beneficial relationship between thermo-mechanical properties with high conductivity. They consist of a lower density than copper, excellent thermal conductivity, low coefficient of thermal expansion (CTE), and better machinability (Rao, 2017). However, Cu-SiC manufacturing techniques carry the predominant challenge of preventing reaction during the densification at a higher temperature between copper and SiC, which dramatically decreases the thermal conductivity (Rao, 2017). Copper (Cu) is capaciously utilized in extravagant applications, such as integrated circuits, electric switches, and electronic packages by virtue of its distinguishable characteristics, such as high electrical conductivity, fatigue resistance, workability and corrosion resistance. However, it retains restricted mechanical properties (Franczak and Karwan-Baczewska, 2017). The copper-based MMCs are under investigation by assorted researchers (Hong, 2011; Shehata, 2009; Moghadam, 2015) for addressing the requirements for their utilization in the functional applications. The key to counterfeit materials with essential mechanical and electrical characteristics is that they should block the dislocation motions with minimizing scattering of conducting electrons to certain acceptable levels (Duarte and Ferreira, 2016). In mainstream, ex-situ or in-situ methods (Tjong, 2013) have been used as different approaches to disperse reinforcement particles in the copper matrix to improve its mechanical properties. The quantity of reinforcement appended to the metal matrix will remarkably influence the microstructure and functional characteristics of the composites (Franczak and Karwan-Baczewska, 2017). The necessary properties can be achieved by varying the amount of weight/volume fraction of the reinforcement material particles (Geim and Novoselov, 2007). The homogeneous distribution of the reinforcement particles is the most consequential factor in obtaining the composites with improved mechanical properties (Pai et al., 2004). The particle size of the reinforcements has an unassailable effect on the mechanical properties of composites. Thus, the preference must be given to the nanosized particulates as reinforcing materials (Geim and Novoselov, 2007).

Properties of Copper-Based MMCs (Ramkumar, 2018)

- Low coefficient of thermal expansion
- High stiffness (modulus of elasticity)
- Good electrical conductivity
- High thermal conductivity
- Good wear resistance

Table 6 states the quantitative values of properties of Cu based MMCs in a tabular structure.

Applications of Copper-Based MMCs

- Copper MMC composites, such as Glidcop, retains the characteristics of copper material even at higher levels of temperatures and radiation. It is deployed as radio-frequency quadrupoles (RFQs) in particle accelerators.

Table 6 Mechanical properties of copper MMC

Property	Units	Values
Density	g/cm^{-3}	2.85
Elongation at break	%	6
Tensile modulus	GPa	100
Tensile strength – longitudinal	MPa	610
Volume fraction of SiC	%	17
Yield strength	MPa	400

Note: Franczak, A., Karwan-Baczewska, J., 2017. Metallurgy and Foundry Engineering 43.



Fig. 13 “Green Bullet” produced with copper jacketed tungsten. Reproduced from Collins, J.M., Mikko, D., 2000. A technical report by Don Mikko, US. Association of Firearm and Tool Mark Examiners Journal. Available at: <http://www.firearmsid.com/Feature%20Articles/GreenBullets/GreenBullets.htm>.

- In electronics, because of its very high thermal conductivity, the copper-silver alloy matrix consisting of diamond particles 55% by volume known as Dymalloy is deployed for the application of multi-chip modules, which demands high-power, high-density materials.
- For high-temperature structural radiators, the Gr/Cu MMCs with high thermal conductivity are deployed.
- Cu based MMCs are used for fabricating hybrid modules, electronic relays, electricity conducting springs, and other electronic components (Ramkumar, 2018).
- The multi-node attachment for connecting trusses is made of copper-based MMCs (Rawal, 2001).
- The volcanic tuff and copper powder were mixed in a turbula rotary mixer; blends were prepared to contain 5, 15 and 30 volumetric percentages of tuff respectively and were examined. The powder metallurgy process was used for manufacturing it. This Cu based MMC is used in nozzle tips of resistance welding electrodes (Mikuła *et al.*, 2015).
- The American military researchers have developed a lead-free projectile as lethal standard 5.56 mm. It is known as “GREEN BULLET,” as shown in Fig. 13. It replaced the copper-jacketed lead core with copper jacketed tungsten tin or nylon core. This will have a positive impact on the growing environmental and health impacts of lead (Collins and Mikko, 2000).

EDM copper tungsten electrode is manufactured with powder metallurgy to take advantage of a combination of EDM properties of tungsten and copper. Excellent wear properties have been displayed by tungsten and copper integrates combining high electrical conductivity of copper and a high melting point of tungsten together.

Other Applications

The New York University (NYU) polytechnic school of engineering delineated that researchers at the school have given a practical exhibition and explanation of a freshly new MMC that as light as it can float on water (Fig. 14). Researchers have postulated that a boat/ship produced with such lightweight composites will never sink, except if some damage is caused to its structure. This newly discovered material can also assure the improvement in automotive fuel economy since it efficiently combines lightweight characteristic with the heat resistance (Anon 4, 2014; Business Communications Company, 2006).

Compared to a water density of 1.0 g/cc, a composite material containing magnesium alloy as a matrix reinforced with silicon carbide hollow particles has a density of 0.92 g/cc. It has been developed in co-operation with Deep Springs Technology (DST, Toledo, OH, US). The university also reveals that the technology used for the new composite materials can be put as prototypes for testing within three years as it is very close to maturation. Amphibious vehicles, such as the ultra heavy-lift amphibious connector

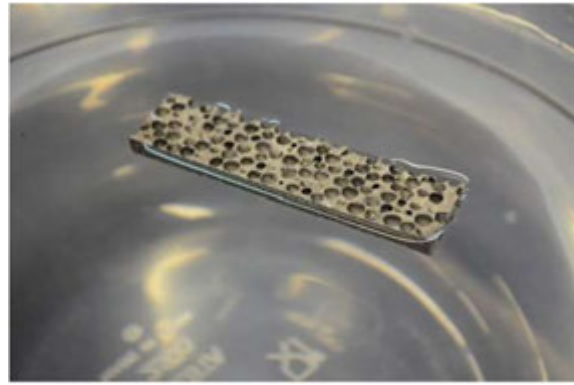


Fig. 14 MMCs that floats has potential in automobile and marine applications.

Table 7 Mechanical and tribological properties of self-lubricating metal matrix composites

Matrix	Self-lubricating phase	Mechanical Properties	Tribological properties
Al-16Si-5Ni	Graphite (5 wt%)	–	In fully lubricated condition, coefficient of friction (COF) = 0.06 against steel
Al-Al ₂ O ₃	TiB ₂	Yield stress = 52.8 ± 1.2 MPa	COF = 0.38 against stainless steel
AA6061	Graphene (15 vol%)	Young's modulus = 50 GPa	COF = 0.2 against steel
TiAl	Grpahene	–	COF = 0.35 against Si ₃ N ₄
Copper	Carbon nano tube (16 vol%)	Hardness (Rockwell P) = 19.8	COF = 0.1 against steel
Al	Graphene (1 wt%)	Hardness (Rockwell F) = 97	COF = 0.25 against steel

Note: Omrani, E., Moghadam, A.D., Algazzar, M., Menezes, P.L., Rohatgi, P.K., 2016. The International Journal of Advanced Manufacturing Technology 87 (1–4), 929–939. Moghadam, A.D., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2016. Tribology Letters 62 (2), 25. Wozniak, J., Kostecki, M., Cygan, T., Buczek, M., Olszyna, A., 2017. Composites Part B: Engineering 111, 1–9. Xu, Z., Shi, X., Zhai, W., *et al.*, 2014. Carbon 67, 168–177. Chen, W., Tu, J., Wang, L., *et al.*, 2013. Carbon 41 (2), 215–222. Tabandeh-Khorshid, M., Omrani, E., Menezes, P.L., Rohatgi, P.K., 2016. Engineering Science and Technology, an International Journal 19 (1), 463–469.

(UHAC), developed by the U.S. Marine Corps might particularly get benefitted from the high buoyancy to weight ratio offered by the new synthetic foams. Nikhil Gupta, a professor in the Department of Mechanical and Aerospace Engineering at NYU School of Engineering and his co-author of the study, says, “This advancement of feathery light MMCs can swing the pendulum back in approbation of metallic materials. The ability of metals to prolong elevated temperatures can be a huge headway for these composites in engine and exhaust components”. The lightweight SiC hollow spheres were produced and deployed through DST. A single sphere’s shell can successfully undergo the pressure of more than 25,000 psi before it gets ruptured, which is 100 times to the maximum pressure created in a fire hose. The hollow particles also provide impact protection to the synthetic foam because each shell acts as an energy absorber during the fracture phenomenon. The composite can be customized with respect to density and other characteristics by varying number of shells into the metal matrix according to the necessity of the application. This concept can also be deployed with other magnesium alloys that are inflammable. NYU also presumes that the new composite consists of potential applications in boat flooring, automobile parts, and buoyancy modules, along with vehicle armor. The research is being carried out in collaboration with the U.S. Army Research Laboratory.

Self-Lubricating Composites (SLC)

In sliding application, liquid or grease-based lubricants are used to facilitate relative motion between components and to minimize friction and wear. These lubricants can separate the surfaces without forming any asperity junctions (Menezes *et al.*, 2018). However, the use of liquid lubricants functionality reduces in extreme environments, such as vacuum, radiation, pressure, and temperature. At such extreme conditions, solid lubricants, such as MoS₂, hBN, graphene, and graphite, etc., are utilized. Direct application of the solid lubricants is challenging because it is difficult to maintain a uniform layer of solid lubricants between the sliding parts. To overcome this issue, SLC materials have been developed. SLC materials are hybrid composite materials where more than two types of reinforcements are incorporated in the matrix. One type of reinforcement, which is generally a hard phase (usually ceramic) enhances the physical properties of the matrix, such as strength, stiffness, etc., while the other type of soft reinforcement (solid lubricant) enhances the lubricating properties, such as reduces friction and wear. The solid lubricants have been effective in enhancing the tribological properties in metal, polymer, and ceramic matrices (Omrani *et al.*, 2017; Kasar and

Menezes, 2018; Malaki *et al.*, 2019). When the material is sliding against each other, the material gets wear against the counter surface. The solid lubricant particles embedded in the matrix will be exposed to the surface, thereby keeping the surface lubricated. A distinctive feature of self-lubricating composites is that the wear particles formed on the contact surface acts as solid lubricants, and it can reduce the friction coefficient and wear rate. Casting or powder metallurgy techniques can be used to manufacture self-lubricating metal matrix composites. A classic example of this type of SLC is the gray cast iron; it utilizes a hard iron matrix with dispersed lubricating graphite flakes. Common types of matrices used for the manufacturing of SLC are aluminum, copper, nickel, magnesium, silver, and its alloys. Implementing SLC into different mechanical systems is a solution to reduce the use of external toxic petroleum-based lubricants in a way to support the environment and to reduce energy dissipation in industrial components for strategies toward energy efficiency and sustainability. Some of the SLC materials are listed in Table 7, along with their mechanical and tribological properties:

Conclusions

The properties of the MMCs depend upon the type of reinforcements and the production processes, which influence its applications. Every year the use of MMCs is increasing, but more percentage of applications are observed in the ground transportation sectors, electronic/thermal management, and other areas. The aluminum-based MMCs have wide applications as compared to the other MMCs, which are at significant interests among the researchers. The MMCs have broad applications in the automotive sector, due to the better strength and other mechanical properties at elevated temperatures, as compared to its weight. The titanium-based MMCs have more applications in the biomedical sector due to its chemical stability with the other improved qualities. Only the aluminum-based MMCs are of booming interest amongst researchers, but the other MMCs lack the research and applications, which gives a potential topic for further investigation. There is advancement in the metal matrix nano-composites for its applications in the advanced armor system in the military department.

References

- Air Force Technology, 1997. F-22A Raptor Advanced Tactical Fighter, USA. Available at: <https://www.airforce-technology.com/projects/f22/>.
- Allison, J.E., Cole, G.S., 1993. Journal of the Minerals. 19–24.
- Anderson, R.E., 1998. Titanium matrix composite turbine engine component consortium. In AMPTIAC Newsletter. AMPTIAC.
- Anon 4, 2014. Available at: <http://tungsten-copper-alloy.blogspot.com/2014/>.
- Bechmann, F., Fallbohmer, P., Stauber, R., Rauber, C., 2007. SAE Technical Paper.
- Business Communications Company, 2006. RGB-108N Metal matrix composites in the 21st century: Markets and opportunities. Available at: http://www.bccresearch.com/market_research/advanced_materials/metal_matrix_composites_market-avm012d.html.
- Collins, J.M., Mikko, D., 2000. A technical report by Don Mikko, US. Association of Firearm and Tool Mark Examiners Journal. Available at: <http://www.firearmsid.com/Feature%20Articles/GreenBullets/GreenBullets.htm>.
- Connell, T.O., 1973. Production of Titanium Aluminide Products, AFWAL-TR-83-4050, WPAFB. Ohio.
- Dasgupta, R., 2012. ISRN Metallurgy. 1–14. (594573).
- Duarte, I., Ferreira, J.M., 2016. Materials 9 (2), 79.
- Elmarakbi, A., 2014. Advanced Composite Materials for Automotive Applications: Structural Integrity and Crashworthiness. John Wiley & Sons Ltd.
- Franczak, A., Karwan-Baczewska, J., 2017. Metallurgy and Foundry Engineering. 43.
- Geim, A.K., Novoselov, K.S., 2007. Nature materials 6 (3), 183.
- Guo, Z.X., Derby, B., 1995. Progress in Materials Science 39, 411–495.
- Haghshenas, M., 2016. Metal-Matrix Composites. University of Waterloo; Elsevier Inc.
- Hayat, M.D., Singh, H., He, Z.C., 2019. Composites: Part A.
- Holley, R., 2013. The Great Metal Tube in the Sky.
- Hong, E., 2011. Wear 270 (9–10), 591–597.
- Hunt, H.W., Miracle, D.B., 2001. Automotive applications of metal-matrix composites. In: Composites, 21. ASM International. pp. 1029–1032.
- Kasar, A.K., Menezes, P.L., 2018. The International Journal of Advanced Manufacturing Technology. 1–21.
- Kevorkjian, V.M., 1999. Journal of Metals. 54–58.
- Leyens, C., Peters, M., 2003. Titanium and Titanium Alloys: Fundamentals and Applications. John Wiley distributor.
- Li, S., Sun, B., Imai, H., 2013. Composites Part A: Applied Science and Manufacturing 48, 57–66.
- Liu, Y., Chen, L.F., Tang, H.P., *et al.*, 2006. Materials Science and Engineering: A 418 (1–2), 25–35.
- Lu, L., 2004. Science 304 (5669), 422–426.
- Malaki, M., Xu, W., Kasar, A.K., *et al.*, 2019. Metals 9 (3), 330.
- Mavhungu, S.T., 2017. Procedia Manufacturing 7, 178–182.
- Menezes, P.L., Rohatgi, P.K., Omrani, E., 2018. Self-Lubricating Composites.
- Mikulá, M., Lach, M., Kowalski, J.S., 2015. Metab 54 (1), 143–146.
- Miracle, D.B., 2005. Composites Science and Technology. 2526–2540.
- Miyamoto, N., 2013. Automotive Coatings and Applications 5A.
- Moghadam, A.D., 2015. Composites Part B: Engineering 77, 402–420.
- Moonaa, G., Waliab, R.S., Rastogib, V., 2018. Indian Journal of Pure & Applied Physics 56, 64–175.
- Mustafa, M., Abdulgadir, D.B., 2017. International Research Journal of Engineering and Technology 4 (4).
- Omrani, E., Menezes, P.L., Rohatgi, P., 2017. Tribology and Applications of Self-Lubricating Materials. CRC Press.
- Pai, B.C., Rajan, T.P., Pillai, R.M., 2004. Indian Foundry Journal. 30–39.
- Peng, H.X., 2005. Journal of Materials Science and Technology 21 (5), 647–651.
- Prasad, S.V., Asthana, R., 2001. Tribology Letters. 445–453.

- Rajak, D.K., Pagar, D.D., Kumar, R., Pruncu, I.C., 2019. Journal of Materials Research & Technology 8 (6), 6354–6374. doi:10.1016/j.jmrt.2019.09.068.
- Rajak, D.K., Wagh, P.H., Menezes, P.L., Chaudhary, A., Kumar, R., 2020. Journal of Bio and Tribo-Corrosion 6 (12), doi:10.1007/s40735-019-0305-x.
- Rajkovic, V., Bozic, D., Jovanovic, M.T., 2010. International Journal of Materials Research. 334–339.
- Ramkumar, J., 2018. Manufacturing of Composites, Kanpur, Notes.
- Rao, P.P., 2017. International Journal of Engineering Technology Science and Research 4 (12), 855–864.
- Rashad, M., Pan, F., Asif, M., 2015. Graphene Materials. 153–190.
- Rawal, S., 2001. JOM 53 (4), 14–17.
- Rohatgi, P.K., Weiss, D., Gupta, N., 2006. Journal of Metals. 71–76.
- Salvo, C., Mangalaraja, R.V., Udayabashkar, R., Lopez, M., 2018. Enhanced mechanical and electrical properties of novel graphene reinforced copper matrix Composites. Journal of Alloys and Compounds 777.
- Shehata, F., 2009. Materials & Design 30 (7), 2756–2762.
- Singerman, S., Jackson, J., Kissenger, R.D., *et al.*, 1996. Superalloys. Warrendale, PA: TMS.
- Singerman, S.A., Jeffrey, J.J., 2018. Pratt & Whitney West Palm Beach FL. GE Aircraft Engines.
- Specialty Materials, Inc., F-16 landing brace. Available at: <http://specmaterials.com/f16landingbrace.htm>.
- Stojanovic, B., Ivanovic, L., 2015. Application of aluminium hybrid composites in automotive industry. Tehnicki Vjesnik 22 (1), 247–251.
- Tjong, S.C., 2013. Materials Science and Engineering: R: Reports 74 (10), 281–350.
- Trinh, S.N., Sastry, S., 2016. Processing and properties of metal matrix composites. Mechanical Engineering and Materials Science Independent Study. 10.
- Vijaya Ramnath, B., Elanchezian, C., 2013. Reviews on Advanced Materials Science 38 (2014), 55–60.
- Welsch, G., Boyer, R., Collings, E., 1993. Materials Properties Handbook: Titanium Alloys. ASM International.

Metal Matrix Composites for Automotive Components in Depth Case Study: Development of Automotive Brake Disc

Nanang Fatchurrohman, Universiti Malaysia Pahang, Pekan, Pahang, Malaysia

Shamsuddin Sulaiman, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Nanang Fatchurrohman, Shamsuddin Sulaiman, Metal Matrix Composites for Automotive Components in Depth Case Study: Development of Automotive Brake Disc, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2018, <https://doi.org/10.1016/B978-0-12-803581-8.10487-4>.

Introduction

The increasing demand for fuel efficiency and light weight components in automobile sectors lead to the development of advance material parts with improved performance (Natarajan *et al.*, 2006). A specific class of MMCs which has gained a lot of attention due for its potential is aluminium metal matrix composites (Al-MMCs). Al-MMCs have a big potential for several applications in automobile parts. This specific class possesses high wear resistance and high specific mechanical property, 67% lower density than cast iron and three times the thermal conductivity, thus Al-MMCs are ideal materials for the manufacture of lightweight automotive components (Prasad and Asthana, 2004). Initialisation of Al-MMCs application in automotive industry was in car engine, which utilised reinforced Al-MMCs for pistons in the Toyota diesel engine (Chawla and Chawla, 2006a; Evans *et al.*, 2003). Experimental studies have been carried out to evaluate the effect of sliding velocity and applied load on the wear characteristics of Al-MMCs (Rao and Das, 2010) which indicated some potential for application in vehicle braking system.

Automotive braking system is subjected to mechanical and thermal stresses, hence depends on a combination of properties. Thus it is hard to select a material based only on one of these properties. The material applied in brake disc must bear thermal fatigue, moreover it should absorb and dissipate quickly heat generated during braking (Cueva *et al.*, 2003). Although MMCs have been applied for brake disc, the product has not yet been highly produced and used widely for replacement of the existing iron brake disc due to high manufacturing cost for mass production (Miracle, 2005). Therefore, this indicates a potential avenue of further research in the field of MMCs and to identify its potential as a replacement for the existing conventional brake disc.

The consequences of globalisation have essentially changed the nature of world market competition (Priest and Sanchez, 2001). Subsequently, first class companies need to employ the right strategy of product development to stay ahead of the competition. They are required to implement product development (PD) strategy which can deliver product with high performance in terms of time to market, product cost and quality (Durmusoglu and Barczak, 2011). Product development plays an important role in the success of manufacturing enterprise and many researchers have enhanced their understanding to manage it strategically (Ayag and Ozdemir, 2009). Product development is concerned with parallel iterations running in a smooth operation and at the moment most influential paradigm that transpired has been the change from the “over-the-wall” strategy or sequential engineering to philosophy of concurrent engineering (McGrath, 2000). Simultaneous approach is part of concurrent engineering (CE) where it promotes parallel consideration of all design parameters where they were considered sequentially in the past. The previous method of sequential engineering has been considered inefficient, since it causes longer development time, higher cost, lower design quality and generates lower profit (Koufteros *et al.*, 2001).

According to Yang *et al.* (2006) CE stimulates simultaneous approach of design activity and other product development life cycle aspects in one working environment. Thus this would lead to product quality improvement, reduced cost, shortened design cycle, reduced time to market and fulfilled customer expectations (Xu *et al.*, 2007). Meanwhile Winner *et al.* (1988) defined CE as a simultaneous and systematic approach to the integrated design of products and their related processes, including product supports. Thus CE forms the foundation for engineers to develop product by taking into account all components of the product life cycle from conception to disposal, including quality, cost, production detail and user requirement (Hsiao, 2002).

Concurrent engineering is a philosophical strategy signifies simultaneous approach to be implemented in the product development process where a product and its manufacturing plan are developed concurrently, cross-functional activities are performed to achieve integration, and prioritize the customer's requirement in the product development process (Fatchurrohman *et al.*, 2015a,b). CE is a direct philosophy, but it has proven to be a powerful PD strategy (Kayis *et al.*, 2006). Some companies reported to have gained up to 60% reduction in time to market, up to 50% reduction in life cycle costs and a maximum 95% of reduction in engineering change demands as the results of implementing CE (Fine *et al.*, 2005).

In the area of product development the need for integration between design parameters selections has been identified by Lu and Deng (2004), where the majorities of materials selection has not been directly linked with engineering aspect coordination including manufacturing process selection, especially at the early design stage. While, Edwards (2002a,b) outlined that the research of materials in some areas is not always relevant to industrial requirements, i.e., it is not oriented to specific applications. Moreover, Ljungberg and Edwards (2003) highlighted the significance of integrated design of product and materials selection and market-oriented design. Product development is related to the selection of design parameters in the early stages as highlighted by Gironimo *et al.* (2006). Early identification of the optimal parameters is a serious job of the design process in order to satisfy

customers, while the most demanding aspect of the approach depends in the quality evaluation of optimal parameters. Whereas according to [Shai et al. \(2009\)](#), conceptual study determines the principles that govern the product and decisions made at this stage have major effect on the final product quality, cost and market share.

Product development has been an essential activity for the success of product competition especially in the fast growing and fierce competition especially in the automotive industry. The focus of product development research in the automotive industry is directed towards developing and implementing light weight – high strength materials, having main objectives to improve vehicle performance, increase fuel efficiency, reduce emissions and increase vehicle safety at competitive cost. [Fatchurrohman et al. \(2013\)](#) stated that the key of a product success in the market rely on the effectiveness of its product development. Among the advanced materials which fall under this category are metal matrix composites (MMCs) ([Prasad and Asthana, 2004](#)). Metal matrix composites (MMCs) have become an essential class of composite materials, which are intensively utilised in some of the new engineering applications. Metal functions as the primary phase (matrix) and a second phase reinforcement is embedded and distributed to achieve some property improvement. Substantial research has been aimed at the advances of these new materials with excellent strength to weight ratio. MMCs have potentials in various applications because of their very good properties in strength, stiffness, lightweight and high temperature resistance ([Basavarajappa et al., 2006](#)).

Literature Review

Metal Matrix Composites (MMCs)

The future trends in material engineering would be the development of synergy among materials for advanced applications. In line with this, the last few decades have witnessed vast growth of new materials. Conventional monolithic materials have limitations in achieving good combination of strength, stiffness, toughness and density. To overcome these shortcomings and to meet the ever increasing demand of modern day technology, composites are most promising materials of recent interest. It is widely known that metal matrix composites (MMCs) fall under the category of composites materials. These materials are increasingly being used in the automobile, aircraft, and space industries ([Miracle, 2005](#); [Chawla and Chawla, 2006b](#)).

A business assessment by [Swift \(2009\)](#) accounted that the world market for MMCs is growing and used up to 4.1 million kg of materials in 2007 and 4.4 million kg in 2008. Furthermore, it is predicted to increase to 5.9 million kg in 2013, for a compound annual growth rate (CAGR) of 5.9%. The ground transportation sector has the biggest share of the market and used 2.4 million kg in 2008; this should reach 3.2 million kg in 2013, for a CAGR of 5.5%. Electronics or thermal management applications have the second largest share and it used 1.4 million kg of MMCs in 2007, this increased to 1.5 million kg in 2008 and is expected to grow at a CAGR of 6.5% to reach 2.1 million kg in 2013.

MMCs can be defined as materials system attained from the result of physical combination of component materials which remain distinct throughout the fabrication history ([Clyne and Withers, 1995](#)). Unlike conventional alloys, including eutectics or alloys containing precipitates or segregated inclusions, in which various phases present are all formed from homogenous melt during solidification and/or heat treatment. MMCs also conduct heat and electricity, which is important attribute in some applications. In some cases, MMCs can be welded or easily fastened to other metallic components ([Evans et al., 2003](#)). MMCs also offer outstanding properties such as high strength to weight ratio, high torsional stiffness, good corrosion resistance and good tolerance characteristics and versatility to the designer ([Miracle, 2005](#)).

While [Kalpakjian and Schmid \(2010\)](#) compares MMCs with conventional polymer matrix composites, with MMCs having higher elastic modulus, resistance to elevated temperatures, radiation and moisture, higher toughness and ductility, better electrical and thermal conductivity. On the other hand the reinforced material may be difficult to fabricate, and the available experience in use is limited. Other limitation is difficulties in processing parts. Polymer and metal matrix composites thus have rather different characteristics, and thus they also have different fields of application

Matrix Materials

In MMCs system the matrix material acts as the primary phase, having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase in its embedded place. The matrix also acts as the medium to transfer load to reinforcement, protect reinforcement from adverse conditions, and prevents brittle crack propagation ([Groover, 2007](#)). Numerous metals have been used as matrices. Beside aluminium some of the most important metals for matrices are titanium, magnesium, and copper alloys.

Significance of aluminium alloy as matrix material

In this product development study the focus of research is on the selection of aluminium metal matrix composites (Al-MMCs), therefore the reason over its selection will be discussed in this section. Aluminium alloy as matrix material is used because of their low density and excellent strength, toughness and corrosion resistance, it has been used widely in the automotive and aerospace fields ([Torrallba et al., 2003](#)).

Al-alloys provide a good matrix for the development of particulate composites which are less expensive and exhibit high mechanical properties. Reinforcing an aluminium alloy with reinforcement material produces a material that displays physical and

mechanical properties of both the metal matrix and the reinforcement material (Evans *et al.*, 2003). For instance, the toughness and formability of aluminium can be combined with the strength of reinforcement material. On a weight adjusted basis, many aluminium based composite materials can outperform cast iron, steel and many alloys in a wide variety of applications (Seah *et al.*, 2003).

The outstanding strength to weight ratio of Al-MMCs have benefits in the transportation segment such as lower fuel consumption, less noise and lower airborne emissions. Other advantages of Al-MMCs compared to unreinforced materials are greater strength, improved stiffness and reduced weight (Surappa, 2003). Furthermore, Al-MMCs have very good properties for high temperature applications with controlled thermal expansion coefficient, enhanced and tailored electrical performance, improved abrasion, wear resistance and improved damping capabilities (Prasad and Asthana, 2004).

Reinforcement materials

The reinforcement material has stronger properties than the matrix material and reinforcement material must be available in sufficient quantity and at an economical rate. Recent researches are directed towards a wider variety of reinforcements for the range of matrix materials being considered, since different reinforcement types and shapes have specific advantages in different matrices.

MMCs are classified based on the type of reinforcement material used which can be divided into three major categories: Particulate, whiskers or discontinuous fibre, and continuous fibre. The most widely used for reinforcement material is silicon carbide (SiC).

Significance of particulate reinforcement

Particle reinforced composites are inexpensive compared to continuous fibre reinforced composites. Cost is an important and essential parameter, particularly in applications where large volumes are required (e.g., automotive applications). The important properties of particulate reinforcement include suitability for high temperature applications, enhanced modulus, increased thermal stability, better wear resistance and relatively isotropic properties compared to fibre reinforced composites (Chawla and Chawla, 2006a).

Manufacturing process of MMCs

Modern metallurgy uses various methods for fabricating MMCs including various types of casting, processes of powder metallurgy, plastic working, spraying, deposition and many others. The choice of a particular fabrication method is mainly determined by the following factors (Tchubarov *et al.*, 1995):

- (1) Type of source materials of matrix and reinforcing agent;
- (2) The possibility of introducing the reinforcing agent into the matrix without damaging;
- (3) Forming a secure bond at the reinforcing agent-matrix interface;
- (4) Maximum realisation in the material properties of its component;
- (5) Attaining the desired reinforcing agent distribution pattern inside the matrix;
- (6) Combining material fabrication with part manufacture;
- (7) Economic efficiency of the process.

A very important consideration in choosing the method is the availability of the desired equipment and the type of end-product. The selection of suitable process engineering is based on the desired type of quantity and distribution of reinforcement, the matrix alloy and the application. By altering the manufacturing method, the processing and the finishing, as well as by the form of the reinforcement components it is possible to obtain different material properties, although the same composition and amounts of the components are involved. Metal matrix composites can be made by liquid, solid, or gaseous state processes (Surappa, 2003).

In this research the selection of manufacturing process is based on production of MMCs by liquid process. In this process, the particulates are integrated into a molten metallic matrix by means of various techniques.

Conceptual research in MMCs

This section explores conceptual work related to MMCs, although this area of study is still in its early phase. It indicated that conceptual and simulation works are potential avenues to contribute for better understanding of MMCs. There are few research works which have been published in the literature; the following paragraphs review the current studies.

Schoutens and Zarate (1986) had presented conceptual design modelling based upon the representations of structural indices for the selection of MMCs materials as substitutes for conventional materials. Technical criteria and operational and cost criteria are used for design considerations. The relevant material property equations are used to derive structural indices. The performance of metal-matrix composites and conventional material are compared in terms of weight-to-strength ratio, impact resistance, efficiency of columns and plates, flexural rigidity, structural efficiency indices for plates and shells, and the work of fracture.

Fatchurrohman *et al.* (2015a,b) had analysed an approach in lightweight and high strength in automotive components with the used of matrix composites. In particular, they had stated that the aluminium based metal matrix composites (Al-MMCs) have some good expectation as a material for several applications in automotive industry. On the other pressing matters, they had also

determined if the material selection could make an impact to the environment, in terms of recyclability, less energy consumption, minimal or none pollution and others environment related.

Talreja (1995) performed conceptual framework for interpretation of fatigue in MMCs. Fatigue data for different MMCs systems are evaluated with the interpretative framework and some observed trends are clarified. Approaches to fatigue modelling are explained for the different regions of performance interpreted by the fatigue diagram. However, further improvements are necessary for completion of database system including manufacturing information and addition of other material property such as yield strength prediction module.

A conceptual study had been performed by Legzdins *et al.* (1997), through the development of an expert system to support engineers in the selection and design of MMCs. The model consists of a dynamic hypertext interface integrated into an expert system exploring mechanical and thermo-physical property data for matrix alloys and reinforcement materials, MMCs data are stored in databases accessed by the expert system. The system includes information on suitable manufacturing techniques. A case study demonstrating the use of the system for selecting MMCs for cryogenic applications is presented.

Modelling with database sources also performed by Zhang *et al.* (2008a,b), MMCs are classified into heterogeneous composite materials and they included functionally gradient materials with a periodic microstructure, respectively. With the database prototype and the methods developed, designers can not only select the suitable materials from the material database to satisfy their critical design requirements, but also can design and add their own special material property into the database. However, due to the variety of materials, further development, refinement and improvement are needed for the material database.

Zhang *et al.* (2008a,b) have progressed into components design to select suitable or optimal materials for heterogeneous material comprising MMCs in the scope of regions during the design of such a component. Their material compatibility or similarity has to be considered, for which an effective evaluation method of the material similarity is needed. In this work, the definitions, evaluation criteria, and calculation formula deductions of material affinities including physical and chemical affinities are developed and described in detail.

Another component design study was performed based on Axiomatic Design and developed by Chen and Feng (2003). They investigated heterogeneous materials including in this class MMCs materials properties. The procedure started with designing component's configuration according to the performance requirement, then determining material properties in different portions of the component followed by selecting optimal material constituent to satisfy material property requirements and various constraints. Finally optimizing the factors of configuration was based on the material selection. The techniques developed have progressed towards design, where it is a significant progress towards articulation of material properties and manufacturing parameters into product development strategy.

Development on Automotive Brake Disc

Brake disc is a vital part in an automobile from passenger safety point of view. It has a significant role in a vehicle performance due to its concern to reduce or stop a vehicle's motion in a normal or critical condition. Fatchurrohman *et al.* (2013) stated that intensive research had been made to produce lightweight and high performance components, which ultimately lead to fuel efficiency and sustainability. The material properties of the brake disc have a significant task by influencing the thermal conductivity and heat dissipation during vehicle braking (Adebisi *et al.*, 2011). Moreover, the material used for brake disc should possess stable and reliable wear properties with high durability (Maleque *et al.*, 2010).

Gray iron has good thermal conductivity due to the graphite phase, which is an excellent thermal conductor. Cueva *et al.* (2003) investigated the wear resistance of three different types of gray cast iron (GCI) used in brake discs. It was studied and compared with the results obtained with a compact graphite iron (CGI). However, when compact graphite iron was tested with lower applied pressures and same friction forces sustained by the gray iron rotors, CGI presented the same performance, as did the gray cast iron. The major constraint of using CGI or cast iron is the weight factor. The weight of brake components has a significant influence on the handling, driving and steering behaviour of a vehicle. It is therefore of interest to investigate lighter weight alternatives to CGI or cast iron brake discs (Kainer, 2006).

The potential of Al-MMCs as brake disc material

In terms of weight, MMCs brake disc designs have a potential to a 60% reduction when compared to cast iron. In addition, aluminium metal matrix composites (Al-MMCs) rotors have the potential to outperform their gray iron counterparts in terms of their mechanical properties and practical application (Bruski, 2000). According to Fatchurrohman *et al.* (2016), Al-MMCs had gained a lot of attention due to its potential as an advanced material part. Studies performed by Natarajan *et al.* (2006) investigates the wear behaviour of Al-MMCs sliding against automobile friction material has been compared with the conventional gray cast iron. A gradual reduction of friction coefficient with increase of applied load is observed for both cast iron and Al-MMCs materials.

Yang (2003) studied MMCs brake disc using pin-on-disc apparatus against heat-treated steel counter surface, giving emphasis on the parameters such as wear coefficient as a function of applied pressure for alloy and composite for various sliding velocities. Wear coefficient of the alloy was noted to be significantly higher than that of the composite and is suppressed further due to addition of silicon carbide particles and applied pressure.

Sahin (2003) studied the wear rate of the composite and the matrix alloy which has been expressed in terms of the applied load, sliding distance and particle size using a linear factorial design approach. It was demonstrated that the composite exhibited a low wear rate compared to the unreinforced matrix material for both cases.

Uyyuru *et al.* (2006) investigated tribological performance of Al-MMCs against brake pad under dry sliding conditions. It was observed that a heterogeneous layer was formed over the worn surfaces during the wear tests. The presence of “tribo” layer was indicated to cause two phenomena; which are acting as a lubricant layer and source of wear debris. The effect of speed, on the wear rate seems to be less dominant compared to load.

Gultekin *et al.* (2010) had performed a research of sintered copper alloy reinforced with graphite particulates brake pads against cast Al-MMCs brake disc and the effects of applied load on the coefficient of friction have been reported. The experimental results proved that the brake disc and the pad have high wear resistance.

Product Development

Product Development (PD) is crucial in the development and improvement of a new product. Fatchurrohman *et al.* (2012) shows that the process involves a very conceptual selection, in which it is an activity that engage with numerous types of data, including technical customer specifications and current design developments. Marini *et al.* (2016) stated that the general conceptual design are comprises of material selection, design concept and material selection. PD is used to interpret the customer's need and requirement into a product. The initial stage of PD is the most important as it involve the time, cost and others matter related to the production. Poor decision might lead to a huge cost and product failure. The development process can be tasking but ultimately lead to good result that can save time, cost, quality and also improve the performance of the product.

Many tools are developed with each of they own function in evaluating a design concept, which compromise of different effective factors such as the customer's requirement, current market competition and designer intentions and functionability. Some of the tools involve are Quality Function Deployment (QFD), which it used to ensure the customer's voice are engaged throughout the product design and development process, as well as improving the quality. It comprises a matrix of conceptual map that linking the interfunctional planning and communication. The QFD system is categorized into phases of product, process and production planning, as well part deployment. This tool is mainly used in making complex decision in product planning.

Multi Criteria Decision Making (MCDM) consists to Analytic Hierarchy Process (AHP) and Analytic Network process (ANP). AHP is used in expressing the general decision operations by the decomposing a problem into a multilevel hierarchy structure comprises of objective, criteria and alternative. It is effective in breaking down multi-criteria problem in hierarchy way to make decision making. ANP however, is more generalized from AHP, in which it allow interrelationships complex among decisions in levels and attributes. It also requires the opinion of the designer in order to carry out pair-wise comparisons.

Research Methodology

Introduction

The research framework was constructed based on simultaneous approach where parallel activities were stimulated and encompasses the entire product life cycle. Simultaneous approach was applied effectively involving the product and process data management coupled with engineering knowledge. Moreover by implementing simultaneous approach, product design and manufacturing entities are developed to bring new product quickly and reduce defects by iterative and substantive considerations in the early phase of product development process (Hsiao, 2002). By means of early consideration of product information, different phases of the problem could be overcome while at the same time the design parameters are evolving. The proposed framework is referred as Integrated Conceptual Selection (ICS) framework. The proposed ICS framework is portrayed in Fig. 1.

Product investigation

This is the first phase in the product development and it is pivotal in determining the success of a product. Product investigation or commonly known as market investigation is an activity of taking information of current and future trends of customers and external factors such as competition into consideration when making decisions. The use of market information has a positive consequence on the product development (Sethi *et al.*, 2001). Whereas, Cooper (2003) informed that there are products which failed due to incorrect product investigation and market analysis thus unable to meet the customer expectations. Product investigation covers the activity of collecting information from three prominent sources, this include product investigation among users (PI-USER), product investigation from the industry (PI-IND) and product investigation from scientific sources (PI-SCI).

Information was collected from users through review of customer opinions on the product. While industrial information was collected via technical reports and patents from industrial sector. Finally, scientific information was surveyed from research papers and articles from the scientific community. The product investigation regarding brake disc involved a thorough research from various sources including reports. The compilation below summarises the findings from this activity.

- (1) “I wish only I had painted the centre hubs...they have rusted after 5000 miles” (Tire track, 2012).
- (2) “Previous MMCs brake rotors were prone to “cook” or even crack under track use” (Forum Lotus, 2012)

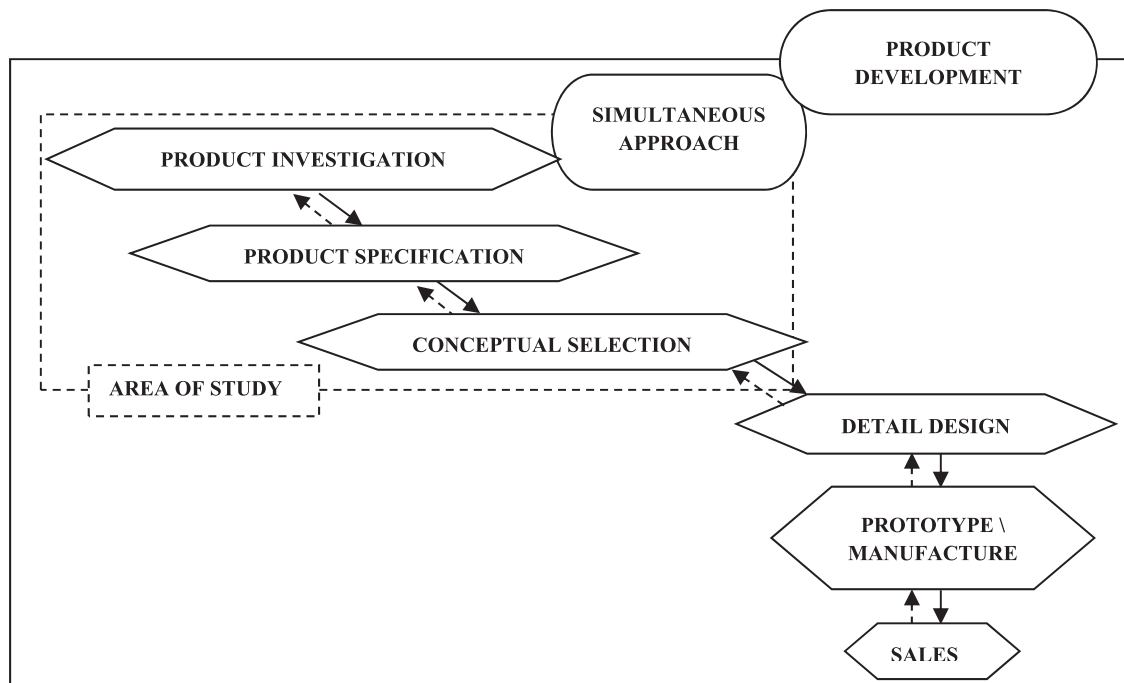


Fig. 1 Integrated Conceptual Selection framework.

- (3) "The weight reduction is unsprung weight...has the potential to improve handling and ride quality as well as improve fuel economy and hard braking performance" (Design News, 2012).
- (4) The most appropriate material for a brake rotor is ideally having rubbing surfaces which operates at a significantly reduced temperature range (Topouzian and Riley, 1996).
- (5) Increased stiffness. Management of thermal expansion. Improved wear resistance. Improved high temperature. High performance vibration damping. Weight reduction (GE Engineering Materials, 2012).
- (6) Stable frictional behaviour over wide range of temperatures. High heat removal. Dimensional stability to reduce vibrations effect. High corrosion resistance to de-icing compounds. High durability. High wear resistance. Lightweight. Overall cost competitiveness (Wall et al., 2006).
- (7) Low pollution rates and low in energy consumption during manufacture, assembly, usage and reprocessing. The material for brake disc must be recyclable (Bakkelund and Storen, 2010).
- (8) Able to sustain torque loads from braking. Stable frictional behaviour at service temperatures. High heat absorption. High thermal conductivity. Excellent machine-ability. Inexpensive raw material. Low processing costs (Ihm, 2013).
- (9) The weight of brake mechanism, has a major influence on the handling, driving and steering behaviour of an automobile. It is therefore of interest to investigate lighter weight alternatives to gray cast iron brake rotors (Buschmann, 2006).
- (10) The tendency of brake rotors is to achieve light weight, high mechanical properties and steady-state friction level (Zhang and Feng, 2011).
- (11) Reinforcements of hard ceramic particles, in ductile metallic matrices can produce composites with considerably higher stiffness and yield strength compared with the unreinforced matrix alloys (Mazahery and Shabani, 2012).
- (12) For the success of MMCs application, cost is the key factor for wider application in modern industry, although potential benefits in weight saving, increased component life, and improved recyclability should be taken into account (Hashim et al., 2001).
- (13) The wear property of MMCs was found to be low, because of the presence of the hard particles present in the MMCs which acts as the load bearing member and abrasive nature (Gultekin et al., 2010).

The information collected from the product investigation was translated and mapped into product performance indicators. It has been identified five significant product performance indicators as illustrated in Fig. 2. The complete mapping is presented in the Appendices. Moreover, these indicators acted as a basis to develop the product specification which is elaborated further in the next section.

Product specification

The mapping between product performance indicators into product specifications showed a direct correlation could be drawn and thus the product specification was identified after the evaluation of product investigation. It was considered as a technical document organised early in the product development which acts as a requirement standards necessary for product design. According to Pugh (1991) product design specifications could be classified into several items, such as, performance, environment, maintenance, and service

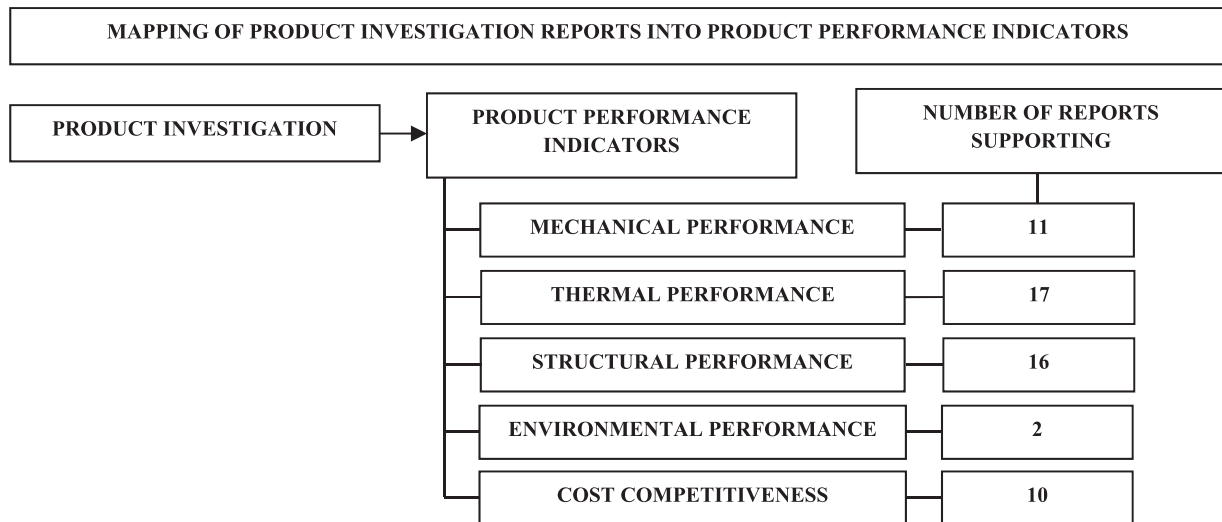


Fig. 2 Product performance indicators.

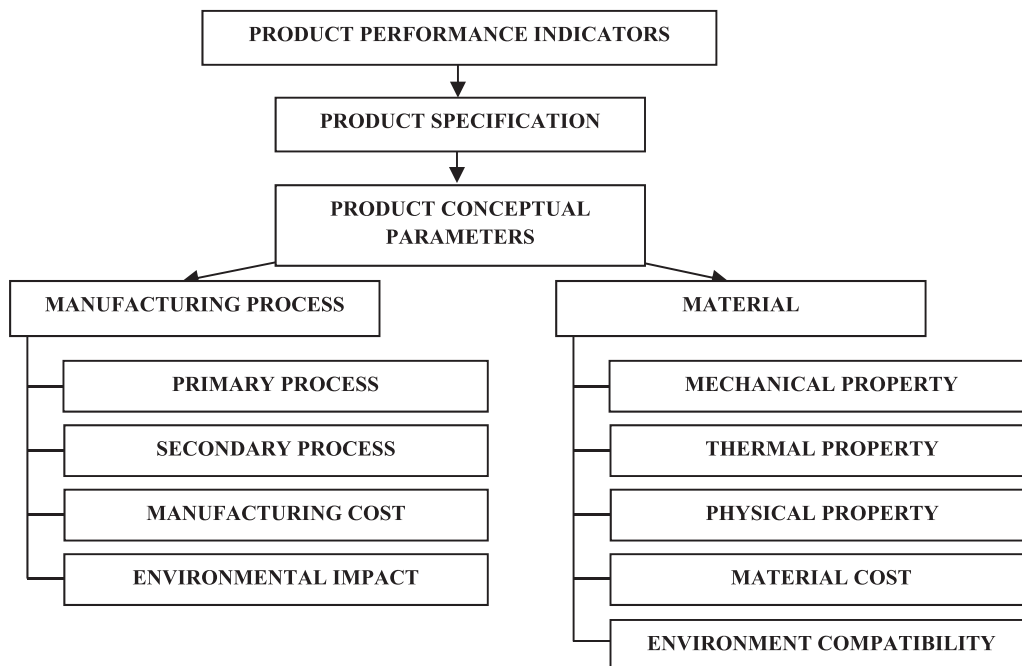


Fig. 3 Product conceptual parameters.

life. However, in this framework the product design specifications were merged and classified into two major design parameters which have the most influence on the outcome of conceptual design. By identifying the product specifications, it enables a concurrent and comprehensive consideration of all design aspects. In this study the product specification was translated into nine sub-parameters under concept parameters of manufacturing process and material as shown in Fig. 3.

Concurrent network

This section discusses in detail the concurrent network (CN) as part of the new MCDM technique. The CN phase combines concurrent or simultaneous approach and ANP procedure. The strategy was applied in a generic framework for synchronised considerations of information from product investigation and product specification to obtain the product performance. Furthermore, concurrent approach (CA) was used for decomposition of product performance into conceptual aspects which were the manufacturing process and material parameters. The parameters were linked into a network, where product performance and design parameters were analysed and identified each performance's influence to the concept parameters. Then the sub-concept parameters were analysed for their interdependence relationships. This was the reason why ANP was used to perform interaction

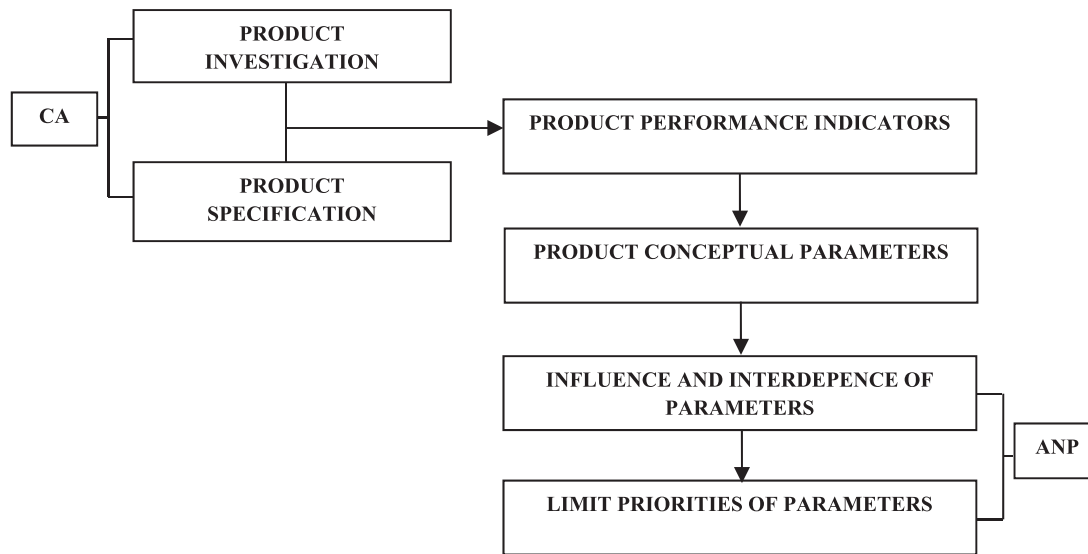


Fig. 4 The work flow of concurrent network.

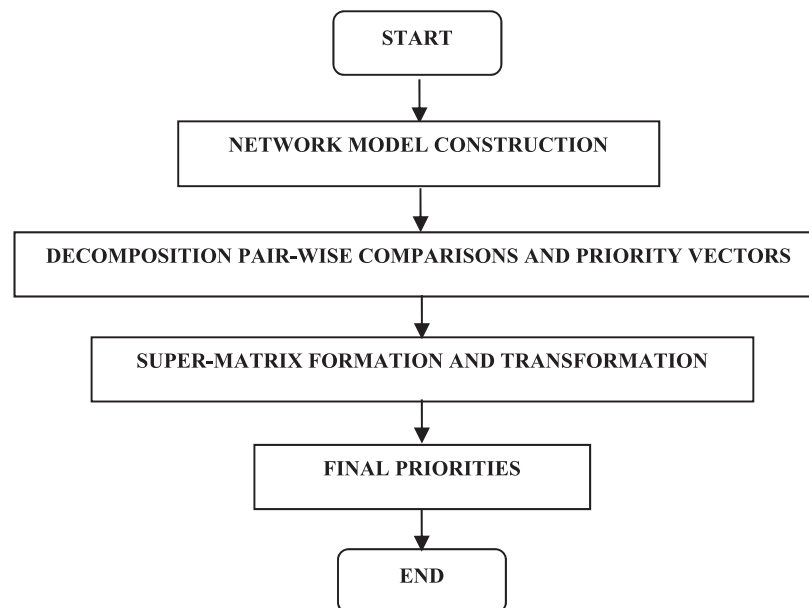


Fig. 5 The work flow of analytical network process.

and interdependence ratings among various parameters in conceptual design clusters. Moreover, pair-wise comparisons were performed to compare concept parameters and sub-concept parameters. The final result from CN analysis was the global and local weights for each sub concept parameters. For further clarification, [Fig. 4](#) depicts the work flow of CN method.

Analytical network process

Analytical network process (ANP) method involves a number of logarithm steps ([Lee et al., 2009a,b](#)). [Fig. 5](#) explains how these steps were taken to analyse interactions between the product parameters. In this study, Super Decision™ and Microsoft Excel™ commercial softwares were used to perform the ANP calculations.

(1) Network model construction

- (a) The conceptual design problem was decomposed into a network where nodes correspond to concept parameter clusters. Connections between clusters were established and loop arrows symbolised relationships between elements inside a cluster ([Fig. 6](#)).

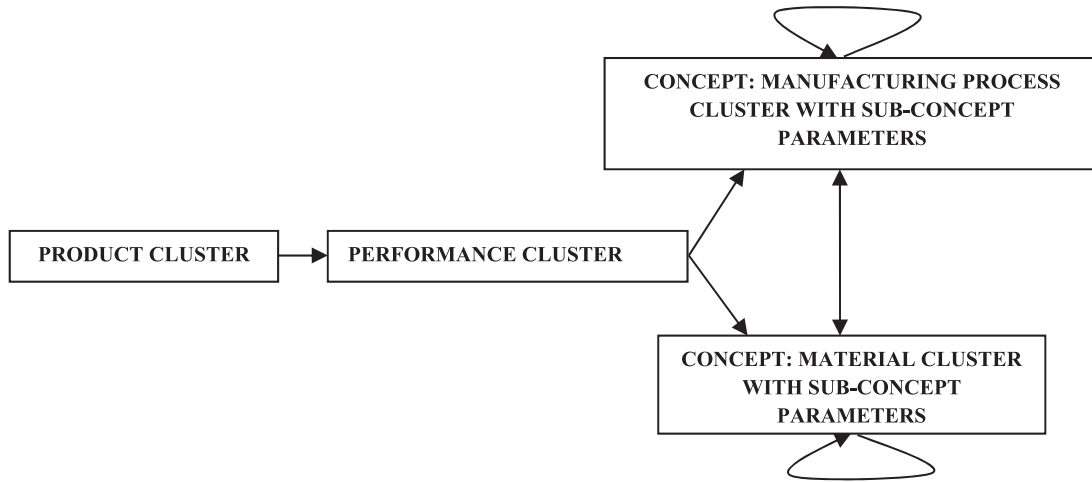


Fig. 6 Cluster network structure.

- (b) Identify elements of sub concept parameter in a cluster which may influence some or all the elements of any other cluster. The relationships among sub concept parameters in the same concept parameter cluster also could exist and connected.
- (2) Pair-wise comparisons and priority vectors
 - (a) Elements of sub concept parameter in each concept parameter cluster were compared pair-wisely with respect to their impacts on an element in same the cluster.
 - (b) In addition, pair-wise comparisons were made for interdependency among elements outside clusters. Cluster weights were required to weight the super-matrix at the next phase, clusters were also compared pair-wisely with respect to their impacts on each cluster.
- (3) Super-matrix formation and transformation
 - (a) The local priorities were entered into the appropriate columns of a super-matrix, which was a partitioned matrix where each segment represents a relationship between two elements within a cluster and two elements in different clusters.
 - (b) The super-matrix of a system of N clusters is described as the following: C_k is the k th cluster ($k = 1, 2, \dots, N$) which has n_k elements denoted as $ek_1, ek_2, \dots, ek_{n_k}$. As inferred in Eq. (1), a matrix segment, W_{ij} , represents a relationship between the i th cluster and the j th cluster. Each column of W_{ij} is a local priority vector obtained from the corresponding pairwise comparison, representing the importance of the elements in the i th cluster on an element in the j th cluster (Saaty, 2004a, b).

$$\begin{array}{ccccccc}
 & C_1 & \cdots & C_k & \cdots & C_N & \\
 & e_{11} \cdots e_{1n_1} & \cdots & e_{k1} \cdots e_{kn_k} & \cdots & e_{N1} \cdots e_{Nn_N} & \\
 C_1 & e_{11} & & & & & \\
 & \vdots & & & & & \\
 & e_{1n_1} & & & & & \\
 & \vdots & & & & & \\
 & e_{k1} & & & & & \\
 w = C_k & \vdots & \left(\begin{array}{cccc} w_{11} & \cdots & w_{1k} & \cdots & w_{1N} \\ \vdots & & \vdots & & \ddots & \vdots \\ w_{k1} & \cdots & w_{kk} & \cdots & w_{kN} \\ \vdots & & \vdots & & \ddots & \vdots \\ w_{N1} & \cdots & w_{Nk} & \cdots & w_{NN} \end{array} \right) & & \\
 & e_{kn_k} & & & & & \\
 & \vdots & & & & & \\
 & e_{N1} & & & & & \\
 C_N & \vdots & & & & & \\
 & e_{Nn_N} & & & & &
 \end{array} \quad (1)$$

- (c) Then, the supermatrix was transformed into the weighted supermatrix each of whose columns sums to one. This 'column stochastic' feature of the weighted supermatrix allows convergence to occur in the limit supermatrix.
- (d) A recommended approach to obtaining the weighted supermatrix was to determine a cluster priority vector for each cluster, which indicates relative importance of influences of other clusters on each cluster. This could be done by conducting pairwise comparisons among clusters with respect to the column cluster.
- (e) The resulting priority vector was then used to weight the matrix segments that fall in the column under the given cluster. The first entry of the vector was multiplied by all the elements in the first matrix segment of that column, the second

entry by all the elements in the second segment of the column and so on. Repeating this weighting procedure for all the column clusters produces the weighted supermatrix.

- (4) Final priorities
 - (a) When the super-matrix covers the whole network, the final priorities of elements were found in the corresponding columns in the limit centrality by raising the all the variables in the weighted super-matrix to powers by multiplying it times by itself.
 - (b) The reason for this was to capture the transmission of influence along all possible paths of the super-matrix. The entries of the weighted super-matrix represent the direct influence of any element on any other element, but an element can influence a second element indirectly through its influence on a third element that has the direct influence on the second element.
 - (c) Such one-step indirect influences were captured by squaring the weighted super-matrix, and two-step indirect influences were obtained from the cubic power of the matrix, and so on.
 - (d) Raising the weighted super-matrix to the power $2k + 1$, where k is an arbitrarily large number, allow convergence of the matrix, which means the row values converge to the same value for each column of the matrix. The resulting matrix is called the limit centrality matrix, in this study it is represented by the limit centrality table.

Results and Discussion

Concurrent Network

The first part of the conceptual design is the concept selection by using concurrent network (CN) which combines CE strategy and ANP method. In this phase CE strategy was implemented by simultaneous consideration and decomposition of product performance into conceptual parameters which include the manufacturing process and material concept parameters. In this research problem ANP method allowed interaction and feedback between the conceptual parameters thus solving complex situations and represents comparisons in the analysis. The outcomes from CN technique were cluster weights, unweighted supermatrix, weighted supermatrix and limit centrality table (Fig. 7). The cluster matrix contains the weights of the main clusters, whereas, the unweighted supermatrix contains the local priorities derived from the pair-wise comparisons throughout the network.

Then it is followed by the result from the weighted supermatrix which was obtained by multiplying all the variables in concept sub-parameters by the corresponding weight of importance for each concept sub-parameters. The final result in the CN phase is the limit centrality table which was attained by raising the weighted supermatrix to powers by multiplying it times by itself; this table contains the local and global weights of the sub concept parameters.

The first discussion will look into cluster in the CN network which is equivalent to a class, and subclasses correspond to elements of conceptual parameters. In the context of CN, the network model comprised of Product, Performance and Concept Clusters. Thus, the importance of clusters was evaluated with respect to impacts or influences on other cluster. The cluster network was constructed based on the relationships represented in Fig. 8.

Product cluster was solely translated and influenced by the performance cluster. Whereas, comparisons were made between concept clusters, in this investigation the concept clusters were compared with respect to the performance cluster. The result indicates that the two main concept clusters (i.e., manufacturing process and material clusters) have the same weight, i.e., 0.5. This means that the concept parameter clusters have the same influence on the performance cluster.

Analysis of parameters within the cluster was related by an outer dependence where parameters in a cluster can depend on some parameters at another cluster. Outer dependencies are represented by two way connector arrows, therefore parameters in cluster can influence the parameters in the other cluster and vice versa (Milani *et al.*, 2012). Inner dependence refers to the condition when parameters of a cluster influence each other (Percin, 2008). In the network (Fig. 9), the outer dependencies are

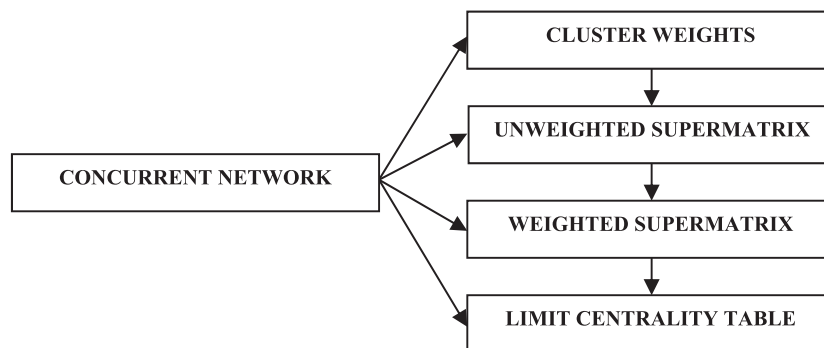


Fig. 7 Concurrent network results.

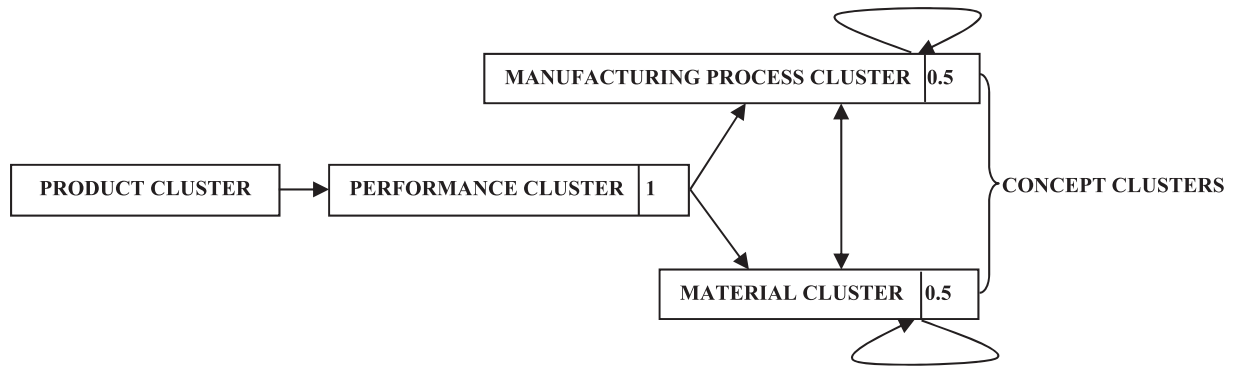


Fig. 8 Cluster network with cluster weights.

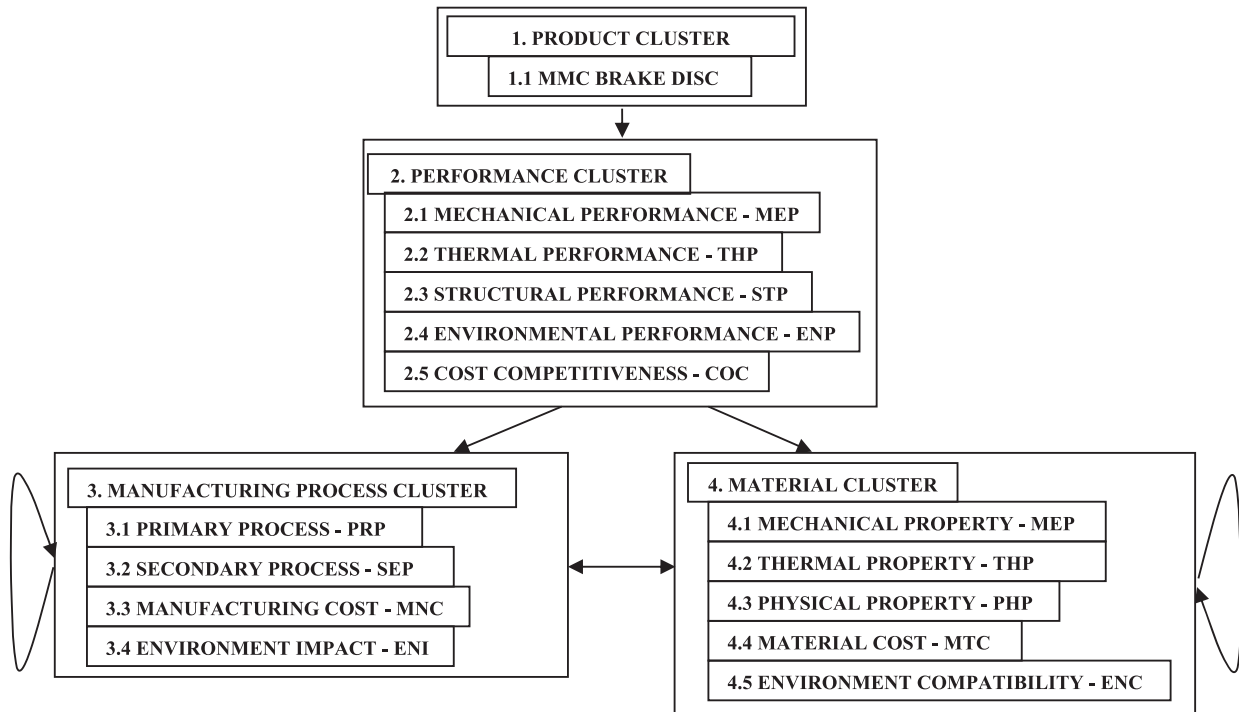


Fig. 9 Cluster network with conceptual parameters.

represented by two-way arrows and inner dependencies by looped arcs. **Fig. 10** shows the analysis as perform in Super Decision™ software.

Unweighted supermatrix

A supermatrix is a two-dimensional matrix of elements by elements under manufacturing process and material concept clusters. The supermatrix was produced from the pairwise comparison matrices of interdependencies and it allows a degree of the effects of interdependence that exists between the elements in the network (Meade and Presley, 2002).

The unweighted supermatrix (USM) (Table 1) contained the result from the pair-wise comparison of all elements for each individual cluster throughout the network, hence the number of comparisons was defined by the number (non-zero) values in the USM and calculated using Eq. (1). The first column A reflects the priorities of the product performance parameters with regards to the goal. The thermal performance (THP) had the highest priority with a score of 0.2123, and then followed by mechanical performance (MEP), thermal performance (THP), structural performance (STP), environmental performance (ENP) having the same priority of 0.1996 and finally cost competitiveness (COC) with a score of 0.1889.

In the following section of the USM refers to the manufacturing process cluster the local priorities. For instance, the sub-concept parameters of primary process (PRP), secondary process (SEP), manufacturing cost (MNC) and environment impact (ENI) with respect to mechanical performance (MEP) were 0.5666, 0.2845, 0.1071, 0.0418. This indicates that primary process (PRP) was

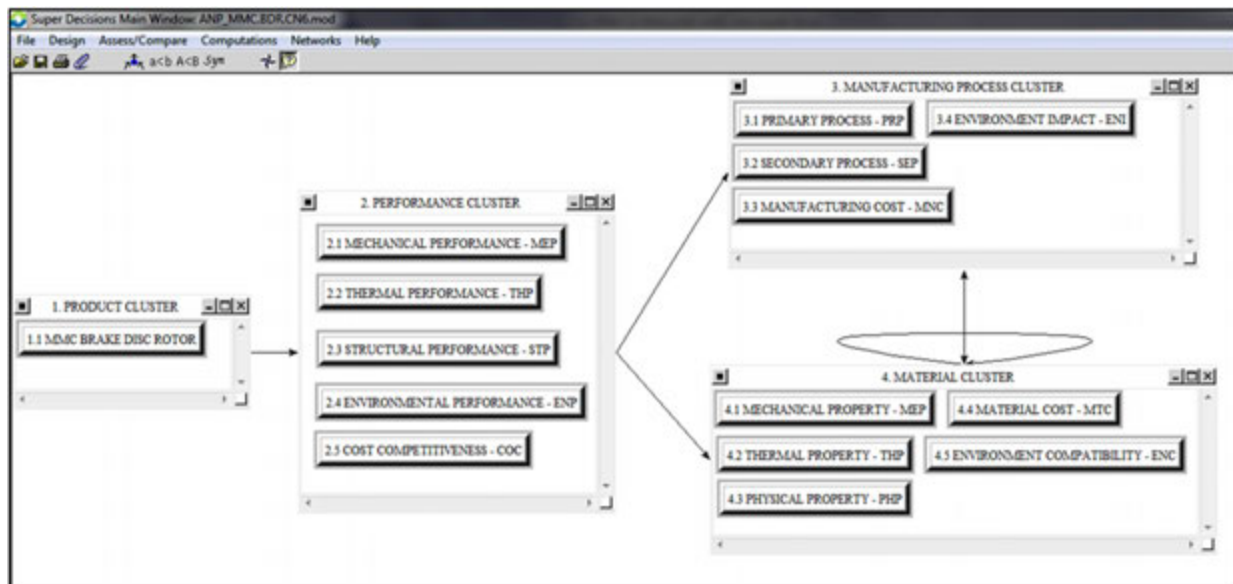


Fig. 10 ANP as performed in Super Decision™.

Table 1 Unweighted supermatrix

			MBD	MEP	THP	STP	ENP	COC	PRP	
Product Performance	1	MBD	0	0	0	0	0	0	0	
	2	MEP	0.1996	0	0	0	0	0	0	
	3	THP	0.2123	0	0	0	0	0	0	
	4	STP	0.1996	0	0	0	0	0	0	
	5	ENP	0.1996	0	0	0	0	0	0	
	6	COC	0.1889	0	0	0	0	0	0	
Manufacturing process	7	PRP	0	0.5666	0.5598	0.531	0.1725	0.2084	0	
	8	SEP	0	0.2845	0.301	0.2986	0.1437	0.1203	0.1429	
	9	MNC	0	0.1071	0.0984	0.1265	0.355	0.6017	0.7143	
	#	ENI	0	0.0418	0.0408	0.0439	0.3288	0.0695	0.1429	
Material	11	MEP	0	0.5869	0.0497	0.5566	0.0667	0.1849	0.5036	
	#	THP	0	0.05	0.6381	0.1146	0.0609	0.1456	0.2526	
	#	PHP	0	0.2425	0.2006	0.243	0.1675	0.1557	0.1511	
	#	MAC	0	0.079	0.0716	0.0598	0.0658	0.2906	0.0464	
	15	ENC	0	0.0416	0.0399	0.026	0.6391	0.2231	0.0464	
		SEP		MNC	ENI	MEP	THP	PHP	MAC	ENC
Product Performance	1	MBD	0	0	0	0	0	0	0	0
	2	MEP	0	0	0	0	0	0	0	0
	3	THP	0	0	0	0	0	0	0	0
	4	STP	0	0	0	0	0	0	0	0
	5	ENP	0	0	0	0	0	0	0	0
	6	COC	0	0	0	0	0	0	0	0
Manufacturing process	7	PRP	0.6491	0.6175	0.6175	0.5671	0.5671	0.5974	0.25	0.0834
	8	SEP	0	0.2969	0.2969	0.2871	0.2871	0.2533	0.25	0.0834
	9	MNC	0.279	0	0.0856	0.111	0.111	0.119	0.25	0.0834
	#	ENI	0.0719	0.0856	0	0.0348	0.0348	0.0304	0.25	0.7497
Material	11	MEP	0.4129	0.2	0.0769	0	0.4045	0.4169	0.25	0.25
	#	THP	0.3641	0.2	0.0769	0.0884	0	0.4169	0.25	0.25
	#	PHP	0.1236	0.2	0.0769	0.4256	0.4337	0	0.25	0.25
	#	MAC	0.0497	0.2	0.0769	0.4265	0.1299	0.1216	0	0.25
	15	ENC	0.0497	0.2	0.6923	0.0595	0.0319	0.0447	0.25	0

more significant to other sub-concept parameters in regards to the mechanical performance (MEP) and then the next priorities were followed by secondary process (SEP), manufacturing cost (MNC) and environment impact (ENI). The priorities of other relationships between manufacturing process parameters and performance parameters can be referred from columns B to F and rows 7–10.

While the inner-dependence within the manufacturing process cluster, for instance in the case of manufacturing cost (MNC) at column I the inner-dependence comparisons of sub-concept parameters refers to primary process (PRP), secondary process (SEP) and environment impact (ENI) with respect to manufacturing cost (MNC) and the results were 0.6175, 0.2968, 0.08563. This means that primary process (PRP) had higher effect and more significant compared to secondary process (SEP) by 2.08 times and to environment impact (ENI) by 7.21 times. While secondary process (SEP) was 3.47 more significant compared to environment impact (ENI) in respect to manufacturing cost (MNC). Whereas, the other significance weights of the interrelationships of sub-concept parameters within the manufacturing process cluster can be referred from column G to column O and row 7 to row 10.

The relationship between material parameters and performance parameters show for instance the local weights of the sub-concept parameters of mechanical property (MEC), thermal property (THE), physical property (PHP), material cost (MAC), environment compatibility (ENC) with respect to thermal performance (THP) were 0.0497, 0.6386, 0.2006, 0.0716, 0.0399. This refers that the mechanical property (MEC) having the highest importance and the most influence to the thermal performance (THP), and followed by sub-concept parameters of thermal property (THE), physical property (PHP), material cost (MAC), environment compatibility (ENC). The complete set of weights referring to other relationships material parameters and performance parameters can be inferred at column B to column F and row 11 to row 15.

Inside the material cluster, the interrelationships between sub-concept parameters were analysed. For example, under the column L – thermal property (THP), the values represent the importance of mechanical property (MEC), physical property (PHP), material cost (MAC), environment compatibility (ENC) with respect to thermal property (THE). The results in sequence were 0.4045 (MEP), 0.4336 (PHP), 0.1299 (MAC) and 0.0319 (ENC); this indicates that the physical property (PHP) had the highest influence to the thermal property (THE) by 1.072, 3.338, 13.59 when compared to mechanical property (MEC), physical property (PHP), material cost (MAC), environment compatibility (ENC) respectively. The next significance of influence to thermal property (THE) in orderly manner was mechanical property (MEC), material cost (MAC) and environment compatibility (ENC). The rest of interdependence relationships within the material cluster are shown in column G to column O and row 11 to row 15.

Weighted supermatrix

The next phase involve the transformation of the USM into the weighted supermatrix (WSM) as in [Table 2](#). It was performed by multiplying each elements of the USM by the corresponding cluster weight.

This was performed in order to obtain the normalised scores for all the elements and hence able to compare each element to another in terms of its priority. The normalised matrix is achieved when the elements have non-zero numbers and the columns add up to one (i.e., column stochastic), it is then referred as the WSM ([Saaty, 2004a,b](#)).

The first column in the WSM was the same as in the USM, it presents the priorities of the performance parameters in regards to the goal cluster. The priorities which referred to the relationship between concept parameters and performance parameters were presented in normalised weight. For instance in column D, which refers to structural performance (STP) the rank of manufacturing process was mostly influenced by primary process (PRP) – 0.2655, followed by secondary process (SEP) – 0.1493, manufacturing cost (MNC) – 0.0633 and environment impact (ENI) – 0.0204. This indicates that the achievement of in the structural performance was influenced mostly by primary process (PRP) quality and the second most influential was the secondary process (SEP). Whereas, in the material conceptual cluster, the most significance influencing the structural performance parameter was mechanical property (MEC) with a score of 0.2783 and followed by thermal property (THE) – 0.5729, physical property (PHP) – 0.1214, material cost (MAC) – 0.02991 and least influential was environment compatibility (ENC) – 0.01302. This interpretation could also be applied to column B to F, row 7–15.

Whereas, the inter-dependence values between the within the manufacturing process parameters and within the material cluster were also normalised. Hence, for example under column secondary process (SEP) the sub-concept parameter which had the strongest relation was primary process (PRP) with priority of 0.3246 followed by manufacturing cost (MNC) – 0.1395 and finally environment impact (ENI) – 0.03597. In the material cluster, the results could also be analysed, for instance the relation under column O – environment compatibility (ENC), this was an interesting results since all the sub-concept parameters i.e., mechanical property (MEC), thermal property (THE), physical property (PHP) and material cost (MAC) have the same importance related to environment compatibility (ENC) with score – 0.125. This indicates that the other sub-concept parameters under the material cluster have the same degree influence to the environment compatibility (ENC). This understanding is applicable to column G to O, row 7–15.

Limit centrality

As the WSM covers the network connections between clusters of product, performance indicator, concept parameters, the final priorities of the manufacturing process parameters and material parameters were ranked and scored for its level of importance. This was done by using the limit centrality table (LCT). The LCT was derived by raising all the values in the WSM to powers by multiplying it times by power $2k + 1$, where k is an arbitrarily large number until it stabilises. Thus, when the columns of values were the same for every column, the LCT had been attained and the matrix multiplication process was stopped ([Saaty and Vargas, 2006](#)). In this case study, the limit centrality represents the overall significance of sub-concept parameters in terms of impacts and

Table 2 Weighted supermatrix

			<i>MBD</i>	<i>MEP</i>	<i>THP</i>	<i>STP</i>	<i>ENP</i>	<i>COC</i>	<i>PRP</i>	<i>SEP</i>
Product Performance	1	MBD	0	0	0	0	0	0	0	0
	2	MEP	0.1996	0	0	0	0	0	0	0
	2	THP	0.2123	0	0	0	0	0	0	0
	2	STP	0.1996	0	0	0	0	0	0	0
	2	ENP	0.1996	0	0	0	0	0	0	0
Manufacturing process	3	COC	0.1889	0	0	0	0	0	0	0
	3	PRP	0	0.2833	0.2799	0.2655	0.0862	0.1042	0	0.3246
	3	SEP	0	0.1423	0.1505	0.1493	0.0719	0.0602	0.0714	0
	3	MNC	0	0.0535	0.0492	0.0633	0.1775	0.3009	0.3571	0.1395
	3	ENI	0	0.0209	0.0204	0.022	0.1644	0.0347	0.0714	0.036
Material	4	MEP	0	0.2935	0.0249	0.2783	0.0333	0.0925	0.2518	0.2065
	4	THP	0	0.025	0.3191	0.0573	0.0305	0.0728	0.1263	0.1821
	4	PHP	0	0.1213	0.1003	0.1215	0.0837	0.0779	0.0755	0.0618
	4	MAC	0	0.0395	0.0358	0.0299	0.0329	0.1453	0.0232	0.0248
	5	ENC	0	0.0208	0.02	0.013	0.3196	0.1116	0.0232	0.0248
			MNC	ENI	MEP	THP	PHP	MAC	ENC	
Product Performance	1	MBD	0	0	0	0	0	0	0	
	2	MEP	0	0	0	0	0	0	0	
	2	THP	0	0	0	0	0	0	0	
	2	STP	0	0	0	0	0	0	0	
	2	ENP	0	0	0	0	0	0	0	
Manufacturing process	3	COC	0	0	0	0	0	0	0	
	3	PRP	0.3088	0.3088	0.2835	0.2835	0.2987	0.125	0.0417	
	3	SEP	0.1484	0.1484	0.1435	0.1435	0.1266	0.125	0.0417	
	3	MNC	0	0.0428	0.0555	0.0555	0.0595	0.125	0.0417	
	3	ENI	0.0428	0	0.0174	0.0174	0.0152	0.125	0.3749	
Material	4	MEP	0.1	0.0385	0	0.2023	0.2084	0.125	0.125	
	4	THP	0.1	0.0385	0.0442	0	0.2084	0.125	0.125	
	4	PHP	0.1	0.0385	0.2128	0.2168	0	0.125	0.125	
	4	MAC	0.1	0.0385	0.2133	0.065	0.0608	0	0.125	
	5	ENC	0.1	0.3462	0.0298	0.0159	0.0223	0.125	0	

Table 3 Limit centrality of conceptual and sub-conceptual parameters

<i>Concept</i>	<i>Sub-concept</i>	<i>Weights</i>	
<i>Parameters</i>	<i>Parameters</i>	<i>Global</i>	<i>Local</i>
Manufacturing process	PRP	0.2087	0.4175
	SEP	0.1050	0.2101
	MNC	0.1244	0.2489
	ENI	0.0618	0.1235
Material	MEP	0.1501	0.3002
	THP	0.1065	0.2129
	PHP	0.1089	0.2178
	MAC	0.0752	0.1505
	ENC	0.0593	0.1185

influences on each other and with regards to the performance parameters, taking into account the direct and indirect influences into consideration. The LCT of nine sub-concept parameters is specified in Table 3. From this process, the global weights were obtained. Next the global weights were normalised by cluster weights to obtain the local weights for each element of sub concept parameters in the network. The value of the local elements was the most important for the next step of the MCDM procedure.

In the manufacturing process cluster the primary process (PRP) parameter has the highest score, which means that this sub-concept parameters was the most important to be considered to achieve the required performance of the product. The ranking was followed by manufacturing cost (MNC), secondary process (SEP) and the last was environment impact (ENI). In the material cluster, the ranking was dominated by mechanical property (MEC), which not an expected result since previously the thermal performance (THP) had the highest weight. This could be explained by other performance parameters which their achievability

were relied more on the mechanical property (MEC) than the other sub-concept parameters. The ranking of other sub-concept parameters was physical property (PHP) followed by thermal property (THE), material cost (MAC) and environment compatibility (ENC).

Conclusions

The research described in this study has been concerned with the material selection and performance using Al-MMCs for brake disc. It was defined with five indicators of product performance, which was then decomposed and analysed into the sub-conceptual parameters of the manufacturing process and material.

The investigation of the dependency and relationship between these parameters were carried out using the ANP method. The results were indicated in the matrices and in the limit centrality table. The cluster matrix indicated the weights for each cluster. The unweighted supermatrix contained the local priorities, while the weighted supermatrix indicated the normalised priorities. Finally, the limit centrality table contained the local and global weights of the sub-conceptual parameters. Also, the product development of MMCs brake disc was performed by means of the Integrated Conceptual Selection (ICS) framework.

Although the results presented in this study have demonstrated the effectiveness of the proposed approach, as well as the new MCDM technique, the local weights of the sub-conceptual parameters will be implemented in the next stage of the analysis, which is to analyse and obtain the ratings of the technical specifications.

References

- Adebisi, A.A., Maleque, M., Shah, Q.H., 2011. Surface temperature distribution in a composite brake rotor. *International Journal of Mechanical and Materials Engineering* 6, 356–361.
- Ayag, Z., Ozdemir, R.G., 2009. A hybrid approach to concept selection through fuzzy analytic network process. *Computers & Industrial Engineering* 56, 368–379.
- Bakkelund, T., Storen, S., 2010. TALAT Lecture 2110.01: Automobile Brake Rotor-LCA in Product Design. Trondheim: The Norwegian Institute of Technology.
- Basavarajappa, S., Chandramohan, G., Rao, K.N., Radhakrishnan, R., Krishnaraj, V., 2006. Turning of particulate metal matrix composites – Review and discussion. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture* 220, 1189–1204.
- Bruski, R., 2000. Justifying aluminium metal matrix composites in an era of cost reduction. In: *Modern Casting*. American Foundry Society, Inc.
- Buschmann, R., 2006. Preforms for the reinforcement of light metals-manufacture, applications and potential. In: Kainer, K.U. (Ed.), *Metal Matrix Composites*. Wiley-Vch.
- Chawla, K.K., Chawla, N., 2006a. Metal Matrix Composites. Springer Publishing.
- Chawla, N., Chawla, K., 2006b. Metal matrix composites in ground transportation. *Journal of the Minerals, Metals and Materials Society* 58, 67–70.
- Chen, K.Z., Feng, X.A., 2003. Computer-aided design method for the components made of heterogeneous materials. *Computer-Aided Design* 35, 453–466.
- Clyne, T., Withers, P., 1995. *An Introduction To Metal Matrix Composites*. Cambridge University Press.
- Cooper, L.P., 2003. A research agenda to reduce risk in new product development through knowledge management: A practitioner perspective. *Journal of Engineering and Technology Management* 20, 117–140.
- Cueva, G., Sinatoro, A., Guesser, W., Tschiptschin, A., 2003. Wear resistance of cast irons used in brake disc rotors. *Wear* 255, 1256–1260.
- Design News, 2012. Serving the 21st Century Design Engineers. Available at: <http://www.designnews.com/> (accessed 19.05.12).
- Durmusoglu, S.S., Barczak, G., 2011. The use of information technology tools in new product development phases: Analysis of effects on new product innovativeness, quality, and market performance. *Industrial Marketing Management* 40, 321–330.
- Edwards, K., 2002a. Linking materials and design: An assessment of purpose and progress. *Materials & Design* 23, 255–264.
- Edwards, K.L., 2002b. Towards more strategic product design for manufacture and assembly: Priorities for concurrent engineering. *Materials & Design* 23, 651–656.
- Evans, A., Marchi, C.S., Mortensen, A., 2003. *Metal Matrix Composites in Industry*. Kluwer Academic Publishers.
- Fatchurrohman, N., Iskandar, I., Suraya, S., Johan, K., 2015a. Sustainable analysis in the product development of Al-Metal matrix composites automotive component. In: Sidik, N.A.C., Samion, S. (Eds.), *Applied Mechanics and Materials* 695. Trans Tech Publications, pp. 32–35.
- Fatchurrohman, N., Marini, C.D., Suraya, S., Iqbal, A.A., 2016. Investigation of product performance of Al-Metal matrix composites brake disc using finite element analysis. In: *Proceedings of IOP Conference Series: Materials Science and Engineering*, 114, p. 012107. IOP Publishing.
- Fatchurrohman, N., Sulaiman, S., Sapuan, S.M., Ariffin, M.K.A., Baharuddin, B.T.H.T., 2013. Generic framework for conceptual design using concurrent engineering strategy. A case study: Advanced material application product development of metal matrix composite component. In: Abdullah, M.M.A.B., Jamaludin, L., Razak, R.A., et al. (Eds.), *Advanced Materials Research* 626. Trans Tech Publications, pp. 99–108.
- Fatchurrohman, N., Sulaiman, S., Sapuan, S.M., Ariffin, M.K.A., Baharudin, B.T., 2012. A new concurrent engineering – Multi criteria decision making technique for conceptual design selection. In: Varatharajoo, R., Abdullah, E.J., Majid, D.L. (Eds.), *Applied Mechanics and Materials* 225. Trans Tech Publications, pp. 293–298.
- Fatchurrohman, N., Sulaiman, S., Sapuan, S.M., Ariffin, M.K.A., Baharuddin, B.T.H.T., 2015b. Analysis of a metal matrix composites automotive component. *International Journal of Automotive and Mechanical Engineering* 11, 2531.
- Fine, C.H., Golany, B., Nasereldin, H., 2005. Modeling tradeoffs in three-dimensional concurrent engineering: A goal programming approach. *Journal of Operations Management* 23, 389–403.
- Forum Lotus, 2012. Lotus talk. Available at: <http://www.lotustalk.com/> (accessed 19.05.12).
- GE Engineering Materials, 2012. Aluminium metal matrix composites. Available at: <http://www.gsengineering.com/> (accessed 20.05.12).
- Gironimo, G.D., Lanzotti, A., Vanacore, A., 2006. Concept design for quality in virtual environment. *Computers & Graphics* 30, 1011–1019.
- Groover, M.P., 2007. *Automation, Production Systems, and Computer-integrated Manufacturing*, third ed. Prentice Hall Press.
- Gultekin, D., Uysal, M., Aslan, S., et al., 2010. The effects of applied load on the coefficient of friction in Cu-MMC brake pad/Al-SiCp MMC brake disc system. *Wear* 270, 73–82.
- Hashim, J., Looney, L., Hashmi, M., 2001. The enhancement of wettability of SiC particles in cast aluminium matrix composites. *Journal of Materials Processing Technology* 119, 329–335.
- Hsiao, S.W., 2002. Concurrent design method for developing a new product. *International Journal of Industrial Ergonomics* 29 (1), 41–55.
- Ihm, M., 2013. Introduction to gray cast iron brake rotor metallurgy. Available at: www.sae.org/events/bce/tutorial-ihm.pdf. (accessed 03.06.13).
- Kainer, K.U., 2006. Basics of metal matrix composites. In: Kainer, K.U. (Ed.), *Metal Matrix Composites*. Wiley-VCH.
- Kalpajian, S., Schmid, S.R., 2010. *Manufacturing Processes For Engineering Materials*, sixth ed. Pearson Education.

- Kayis, B., Arndt, G., Zhou, M., *et al.*, 2006. Risk quantification for new product design and development in a concurrent engineering environment. *CIRP Annals - Manufacturing Technology* 55, 147–150.
- Koufteros, X., Vonderembse, M., Doll, W., 2001. Concurrent engineering and its consequences. *Journal of Operations Management* 19, 97–115.
- Lee, H., Kim, C., Cho, H., Park, Y., 2009a. An ANP-based technology network for identification of core technologies: A case of telecommunication technologies. *Expert Systems with Applications* 36, 894–908.
- Lee, H., Lee, S., Park, Y., 2009b. Selection of technology acquisition mode using the analytic network process. *Mathematical and Computer Modelling* 49, 1274–1282.
- Legzdins, C.F., Samarasekera, I.V., Meech, J.A., 1997. MMCX an expert system for metal matrix composite selection and design. *Canadian Metallurgical Quarterly* 36, 177–202.
- Ljungberg, L.Y., Edwards, K.L., 2003. Design, materials selection and marketing of successful products. *Materials & Design* 24, 519–529.
- Lu, W.F., Deng, Y.M., 2004. A system modelling methodology for materials and engineering systems design integration. *Materials & Design* 25, 459–469.
- Maleque, M., Dyuti, S., Rahman, M., 2010. Material selection method in design of automotive brake disc. In: *Proceeding of World Congress on Engineering*. London, United Kingdom.
- Marini, C.D., Fatchurrohman, N., Azhari, A., Suraya, S., 2016. Product Development using QFD, MCDM and the combination of these two methods. In: *Proceedings of IOP Conference Series: Materials Science and Engineering*, 114, p. 012089. IOP Publishing.
- Mazahery, A., Shabani, M.O., 2012. Influence of the hard coated B₄C particulates on wear resistance of Al-Cu alloys. *Composites Part B: Engineering* 43, 1302–1308.
- McGrath, M.E., 2000. *Product Strategy for High Technology Companies*. McGraw Hill.
- Meade, L.M., Presley, A., 2002. R&D project selection using the analytic network process. *IEEE Transactions on Engineering Management* 49, 59–66.
- Milani, A.S., Shanian, A., Lynam, C., Scarinci, T., 2012. An application of the analytic network process in multiple criteria material selection. *Materials & Design* 44, 622–632.
- Miracle, D.B., 2005. Metal matrix composites – From science to technological significance. *Composites Science and Technology* 65, 2526–2540.
- Natarajan, N., Vijayarangan, S., Rajendran, I., 2006. Wear behaviour of A356/25SiCp aluminium matrix composites sliding against automobile friction material. *Wear* 261, 812–822.
- Percin, S., 2008. Using the ANP approach in selecting and benchmarking ERP systems. *Benchmarking: An International Journal* 15, 630–649.
- Prasad, S., Asthana, R., 2004. Aluminum metal-matrix composites for automotive applications: Tribological considerations. *Tribology Letters* 17, 445–453.
- Priest, J., Sanchez, J., 2001. *Product Development and Design for Manufacturing: A Collaborative Approach to Producibility and Reliability*, second ed. New York: Taylor & Francis.
- Pugh, S., 1991. *Total Design: Integrated Methods for Successful Product Engineering*. Addison-Wesley.
- Rao, R.N., Das, S., 2010. Wear coefficient and reliability of sliding wear test procedure for high strength aluminium alloy and composite. *Materials & Design* 31, 3227–3233.
- Saaty, T., 2004a. Fundamentals of the analytic network process – Dependence and feedback in decision-making with a single network. *Journal of Systems Science and Systems Engineering* 13, 129–157.
- Saaty, T.L., 2004b. Decision making: The analytic hierarchy and network processes (AHP/ANP). *Journal of Systems Science and Systems Engineering* 13, 1–35.
- Saaty, T.L., Vargas, L.G., 2006. *Decision Making with the Analytic Network Process: Economic, Political, Social and Technological Applications with Benefits, Opportunities, Costs and Risks*. Springer Science Business Media.
- Sahin, Y., 2003. Wear behaviour of aluminium alloy and its composites reinforced by SiC particles using statistical analysis. *Materials & Design* 24, 95–103.
- Schoutens, J.E., Zarate, D.A., 1986. Structural indices in design optimization with metal-matrix composites. *Composites* 17, 188–204.
- Seah, K.H.W., Hemanth, J., Sharma, S.C., 2003. Mechanical properties of aluminum/quartz particulate composites cast using metallic and non-metallic chills. *Materials & Design* 24, 87–93.
- Sethi, R., Smith, D.C., Park, C.W., 2001. Cross-functional product development teams, creativity, and the innovativeness of new consumer products. *Journal of Marketing Research* 38, 73–85.
- Shai, O., Reich, Y., Rubin, D., 2009. Creative conceptual design: Extending the scope by infused design. *Computer-Aided Design* 41, 117–135.
- Surappa, M., 2003. Aluminium matrix composites: Challenges and opportunities. *Sadhana* 28, 319–334.
- Swift, C., 2009. Advanced materials: Metal matrix composites: The global market. report code AVM012D. Available at: www.bccresearch.com/report/AVM012D.html (accessed 12.04.12).
- Talreja, R., 1995. A conceptual framework for interpretation of MMC fatigue. *Materials Science and Engineering: A* 200, 21–28.
- Tchubarov, V.M., Zabolotsky, A.A., Kripov, G.A., 1995. Metal matrix fabrication methods. In: Fridlyander, J.N., Marshall, I.H. (Eds.), *Metal Matrix Composites*. Moscow: Chapman and Hall, pp. 61–193.
- Tire track, 2012. Your experts performance on tires and wheels. Available at: <http://www.tirerack.com/> (accessed 19.05.12).
- Topouzian, D., Riley, J.E., 1996. Brake rotor with flow through ventilation: U.S. Patent No. 5,544,726. 13 August 1996.
- Torralba, J., Da Costa, C., Velasco, F., 2003. P/M aluminum matrix composites: An overview. *Journal of Materials Processing Technology* 133, 203–206.
- Uyyuru, R.K., Surappa, M.K., Brusehaug, S., 2006. Effect of reinforcement volume fraction and size distribution on the tribological behavior of Al-composite/brake pad tribo-couple. *Wear* 260, 1248–1255.
- Wall, E., Sullivan, R., Eberhardt, J., 2006. Progress report for high strength weight reduction materials energy efficiency and renewable energy FY 2006, U.S. Department of energy office of freedom car and vehicle technologies, Washington 2006.
- Winner, R.I., Pennell, J.P., Bertrand, H.E., Slusarczyk, M.M., 1988. The role of concurrent engineering in weapons system acquisition (No. IDA-R-338), DTIC Document, Institute for Defense Analyses Alexandria VA.
- Xu, L., Li, Z., Li, S., Tang, F., 2007. A decision support system for product design in concurrent engineering. *Decision Support Systems* 42, 2029–2042.
- Yang, H., Xue, D., Tu, Y.L., 2006. Modeling of non-linear relations among different design and manufacturing evaluation measures for multiobjective optimal concurrent design. *Concurrent Engineering* 14, 43–53.
- Yang, L.J., 2003. The transient and steady wear coefficients of A6061 aluminium alloy reinforced with alumina particles. *Composites Science and Technology* 63, 575–583.
- Zhang, X.J., Chen, K.Z., Feng, X.A., 2008a. Material database for the material design of components made of a multiphase perfect material. *Materials & Design* 29, 1131–1144.
- Zhang, X.J., Chen, K.Z., Feng, X.A., 2008b. An effective evaluation method of material affinity between adjacent material regions of a component for component design. *Materials & Design* 29, 146–153.
- Zhang, S., Feng, S., 2011. Friction and wear performances of brake material dry sliding against a composite with a semi-interpenetrating network structure of ceramics and Al-alloy. *Tribology International* 44, 248–257.

Further Reading

- Albiñana, J.C., Vila, C., 2012. A framework for concurrent material and process selection during conceptual product design stages. *Materials & Design* 41, 433–446.
- Al-Oqla, F.M., Omar, A.A., 2012. A decision-making model for selecting the GSM mobile phone antenna in the design phase to increase over all performance. *Progress in Electromagnetics Research C* 25, 249–269.
- Bayazit, O., Karpak, B., 2007. An analytical network process-based framework for successful total quality management (TQM): An assessment of Turkish manufacturing industry readiness. *International Journal of Production Economics* 105, 79–96.

- Belhocine, A., Bouchetara, M., 2012. Thermal analysis of a solid brake disc. *Applied Thermal Engineering* 32, 59–67.
- Caranddriver, 2013. The power to stop. Available at: <http://www.caranddriver.com/features/the-power-to-stop> (accessed 03.12.13).
- Cdxetextbook, 2012. Cast iron brake disc rotor. Available at: <http://www.cdxetextbook.com/brakes/brake/disc/discrotor.html> (accessed 11.01.12).
- Djassemi, M., 2012. A computer-aided approach to material selection and environmental auditing. *Journal of Manufacturing Technology Management* 23, 1.
- Dow, T.A., 1980. Thermoelastic effects in brakes. *Wear* 59, 213–221.
- Edwards, K.L., 2003. Designing of engineering components for optimal materials and manufacturing process utilisation. *Materials & Design* 24, 355–366.
- Fatchurrohman, N., 2013. Manufacturing process and material selection using modified multi criteria decision making for brake disc. Doctoral dissertation, Universiti Putra Malaysia.
- Ghadimi, P., Azadnia, A.H., Mohd Yusof, N., Mat Saman, M.Z., 2012. A weighted fuzzy approach for product sustainability assessment: A case study in automotive industry. *Journal of Cleaner Production* 33, 10–21.
- Giner-Santonja, G., Aragones-Beltran, P., Niclos-Ferragut, J., 2012. The application of the analytic network process to the assessment of best available techniques. *Journal of Cleaner Production* 25, 86–95.
- Gittelman, M., 2013. Dealing with brake noise problems. Available at: <http://autorepair.answers.com/brakes/dealing-with-brake-noise-problems> (accessed 02.12.13).
- Ipek, M., Selvi, I.H., Findik, F., Torkul, O., Cedimoglu, I.H., 2013. An expert system based material selection approach to manufacturing. *Materials & Design* 47, 331–340.
- Jenab, K., Sarfaraz, A., Ameli, M.T., 2013. A conceptual design selection model considering conflict resolution. *Journal of Engineering Design* 24, 293–304.
- Jiang, Z., Zhang, H., Sutherland, J.W., 2011. Development of multi-criteria decision making model for remanufacturing technology portfolio selection. *Journal of Cleaner Production* 19, 1939–1945.
- Lovatt, A., Shercliff, H., 1998. Manufacturing process selection in engineering design. Part 1: The role of process selection. *Materials & Design* 19, 205–215.
- Maleque, M., Adebisi, A., Shah, Q., 2012. Energy and cost analysis of weight reduction using composite brake rotor. *International Journal of Vehicle Structures & Systems* 4, 69–73.
- Matweb, 2012. SAE J431 automotive gray cast iron, SAE grade G3000. Available at: <http://www.matweb.com/search/DataSheet.aspx> (accessed 10.12.12).
- Meguiarsonline, 2013. Need help with brake rotor choice. <http://www.meguiarsonline.com/forums/showthread.php?26612-Need-help-with-brake-rotor-choice> (accessed 03.12.13).
- Metalandsteel, 2012. Aluminium products. Available at: <http://www.metalandsteel.com/Products/Aluminium.aspx> (accessed 21.04.12).
- Mida, 2013. Electricity Rates Peninsular Malaysia. Malaysian Investment Development Authority. Available at: <http://www.mida.gov.my/env3/index.php?page=electricity-rates> (accessed 11.03.13).
- Pimapsuri, K., Tichkiewitch, S., 2013. Integrated design approach for solving complexity of design problem. *American Journal of Operations Research* 3, 138–146.
- Poudelet, V., Chayer, J.-A., Margni, M., Pellerin, R., Samson, R., 2012. A process-based approach to operationalize life cycle assessment through the development of an eco-design decision-support system. *Journal of Cleaner Production* 33, 192–201.
- Prasad, B., 1998. Review of QFD and related deployment techniques. *Journal of Manufacturing Systems* 17, 221–234.
- Prasad, K., Chakraborty, S., 2013. A quality function deployment-based model for materials selection. *Materials & Design* 49, 525–535.
- Saaty, T.L., Vargas, L.G., 2012. *Models, Methods, Concepts & Applications of the Analytic Hierarchy Process*. Springer.
- Santonja, G.G., Beltran, P.A., Ferragut, J.N., 2012. The application of the analytic network process to the assessment of best available techniques. *Journal of Cleaner Production* 25, 86–95.
- Sigma-Aldrich, 2012. Product catalog. Available at: <http://www.sigmaaldrich.com/catalog/product> (accessed 21.04.12).
- Smith, C., 2013. "Warped" brake disc and other Myths of the Braking System. Available at: <http://www.stoptech.com/technical-support/technical-white-papers/-warpedbrake-discand-other-myths> (accessed 02.12.13).
- TheAA, 2013. Brake wear, corrosion and other problems. Available at: http://www.theaa.com/motoring_advice/general-advice/brakes-discs-drums-pads.html (accessed 02.12.13).
- Thomke, S., Reinertsen, D., 2012. Six myths of product development. *Harvard Business Review* 90, 84–94.
- Yang, S.Y., Girivasan, V., Singh, N.R., Tansel, I.N., Kropas-Hughes, C.V., 2003. Selection of optimal material and operating conditions in composite manufacturing. Part II: complexity, representation of characteristics and decision making. *International Journal of Machine Tools and Manufacture* 43, 175–184.

Application of Metal Matrix Composites in Non-Structural Applications

Mubarak Ali M, TKM College of Engineering, Kollam, Kerala, India

Mohamed Thariq, University Putra Malaysia, Seri Kembangan, Malaysia

Vishwesh Dikshit and Bhudolia S Kumar, Nanyang Technological University, Singapore

© 2021 Elsevier Inc. All rights reserved.

Nomenclature

Al_2O_3 Aluminum Oxide

AlSiC SiC reinforced Aluminum matrix composites

CaF_2 Calcium Fluoride

CNT Carbon Nano Tubes

CoFe_2O_4 Cobalt Ferrite

Cr_3C_2 Chromium(II) Carbide

CT Computed Tomography

EMI Electromagnetic Interference

IGBT Insulated Gate Bipolar Transistor

MMCs Metal Matrix Composites

MoS_2 Molybdenum Disulfide

MRI Magnetic Resonance Imaging

NiCr Nickel Chromium Alloy

NiFe_2O_4 Nickel ferrite

NiTi Nickel Titanium Alloy

NMRI Nuclear Magnetic Resonance Imaging

PTFE Polytetrafluoroethylene

SMA Shape Memory Alloy

SiC Silicon Carbide

WS_2 Tungsten Disulfide

Glossary

Electronic packaging density Number of components per unit volume in an electronic device.

Fretting Wear Type of wear characterized by low amplitude oscillatory motion in the range of few microns.

Heat Sink A device or substance which absorbs unwanted or excessive heat.

Hybrid Composites Composite materials with more than one reinforcement.

Magnetization Measure of density of magnetism.

Monolithic material Material which is composed of only one material.

Specific Stiffness Ratio of elastic modulus to weight.

Specific Strength Ratio of ultimate tensile strength to weight.

Introduction

Materials have been connected and coexisted with humankind for fulfilling diverse needs. Composites are a class of materials, which are made of two or more different monolithic materials to produce a unique blend of properties. There are many composite materials in nature. Wood, bones, silky threads and shell of invertebrates are few examples of composites existing in nature (Ali *et al.*, 2017). There are several classifications of composite materials depending on the criteria used to classify these materials. Most general type of classification is based on the type of matrix materials used in these composites. Based on the type of matrix material used, composites are classified into four types: metal matrix composites, ceramic matrix composites, polymer matrix composites and intermetallic matrix composites. Each type of composite may be divided further into many subtypes depending upon the type of reinforcements used. Composite materials are intrinsically heterogeneous and immiscible when mixed. The matrix and reinforcement remains mechanically separate phases but adequately bonded to each other without forming a solid solution.

Metal matrix composites (MMCs) can be designed and synthesized by reinforcing particulates (particles), fibers or whiskers in an alloy or a metal. These metal matrix composites generally have superior properties and perform better than monolithic alloy or metal in its stated application. The most exciting feature of these metal matrix composites in contrast to monolithic metal/alloy are its versatility in design. They can be tailor made to specific properties by controlling the matrix and reinforcement phases depending upon the requirement of specific application. This feature offers enormous possibilities of designing new metal matrix composites for highly challenging and niche applications. Density, specific stiffness, thermal conductivity, high temperature strength, damping capacity, energy absorption capability and tribological behavior are some of the properties, which can be manipulated, and tailor designed in metal matrix composites.

Metal matrix composites have been highly used in structural applications where low weight combined with high strength and high stiffness is required. They are referred as high specific strength and high specific stiffness of materials. Most notable use of metal matrix composites for its high specific strength/stiffness are in aerospace and automobile industry. Metal Matrices preferable for such applications are aluminum, magnesium and titanium. Another common use of metal matrix composites in high temperature structural applications are in places where high temperature mechanical properties are indispensable. Matrices commonly used in these applications are cobalt and cobalt-nickel. Particulate and discontinuous fiber reinforcements generally results in isotropic properties of the metal matrix composites. The use of continuous fiber reinforcements induce anisotropic properties of the final composites fabricated. The isotropic/anisotropic nature of composite properties is important consideration in structural applications.



Fig. 1 Heat dissipation path in Electronic Packaging.

Most common fabrication methods include solid-state methods (powder metallurgy route), liquid-state methods (squeeze casting, stir casting), semi solid-state methods and in situ fabrication techniques. Advancements in fabrication methods of metal matrix composites and nano reinforcements has expanded the use of these composites to several non-structural applications. The next generation of MMCs are not limited only to load bearing applications but extended to functional applications. MMCs can be designed to inbuilt specific native properties and can be used to perform functions like thermal management in electronic devices, self-repairing functions, self-lubricating functions, electrical and magnetic functions. This article gives a summarized review of applications of metal matrix composites in non-structural applications.

Non-Structural Applications

Thermal Management and Electronic Packaging

In almost all electronic/optoelectronic devices, not all the energy consumed by these devices is converted into useful work. In case of a computer, only a percentage of the electrical energy consumed by it get converted into computing work, light, sound, transmission radio waves and chemical energy in battery. Most of the electrical energy gets converted into heat. Heat sinks used in electronic devices are designed mainly for thermal management in electronic packaging by creating a heat dissipation path (refer [Fig. 1](#) and [Fig. 2](#)). In the past, heat sinks were made of traditional materials like copper, aluminum, copper-molybdenum alloy or copper-tungsten alloy. The ever-increasing density of packaging density and integration level of electronic devices greatly increase the amount of generated waste heat in a small space. The materials used traditionally in heat sinks does not provide efficient thermal management for devices with higher packaging density, low weight and stringent reliability considerations ([Zweben, 1992](#)). Electronic devices with high packaging density demands heatsink with excellent thermal conductivity, thermal expansion coefficient, which matches with that of the electronic component it supports. Novel composite materials has contributed to the improvement of the efficiency of heat sinks.

Metal matrix composites with copper and aluminum as matrices are preferable for heat sink materials. The reason for this is twofold: the thermal conductivity of Al or Cu Matrix composites can be improved by reinforcements with high thermal conductivity and versatility of controlling the coefficient of thermal expansion by adjusting the weight fraction/volume fraction of the reinforcement material. The reinforcements that are used for such heat sink applications are carbon, SiC and diamond either in the form of particles or fibers ([Zweben, 2005](#)). Aluminum matrix based composites are exceptional for thermal management applications because of its low specific weight and high specific thermal conductivity.

Due to low weight and high performance, SiC reinforced aluminum matrix composites has been selected for electronic packaging application in highly demanding avionics industry. With 75% volume fraction of SiC reinforcement, the aluminum matrix composites exhibits low coefficient of thermal expansion ($6-7 \times 10^{-6} \text{ K}^{-1}$) and low density (about 3 g/cm^3) ([Sarno, 2001](#)). However, thermal conductivity of SiC reinforced aluminum matrix composite is not so high to be suitable for high-end applications. Application of SiC/Al particulate composite is limited due to issues in brazing during electronic packaging processes. The brazing temperature of the composite should be in the range of $450-550^\circ\text{C}$ to avoid melting and degradation of mechanical properties. There is a lack of suitable filler metals for brazing in such a temperature range ([QU et al., 2011](#)).

In order to increase the thermal conductivity of aluminum matrix composites, carbon or diamond reinforcements are employed. Diamond reinforcement results in extremely high thermal conductivity where as carbon reinforcement results in a composite with less difficulty in machining ([QU et al., 2011](#)). Typically, these composites are fabricated by liquid infiltration method or powder metallurgy process. Diamond/copper composite with isotropic thermal diffusivity fabricated through high pressure sintering technology was found to have overcome the processing problems faced in the past such as low wettability and unfavorable interfacial reactivity ([Yoshida and Morigami, 2004](#)). $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ nanoparticles reinforced copper matrix composites have been investigated to have exhibited remarkable thermal conductivity (293 W/mK) when compared to SiC reinforced aluminum matrix composites. This novel nanocomposite also has coefficient of thermal expansion, which is matching with GaAs and Si making it a highly assuring material for heat sink application in electronic packaging ([Sanjay et al., 2019](#)).

Application in Microprocessor Lids and Carrier Plates for Power Modules

Thermal management is increasingly inevitable in new generation of microprocessor assemblies with high clock speeds and device density. The thermal management solution include a lid or heat spreader. The lid keep contact with the microprocessor and transfer the heat from the packaging assembly (refer [Fig. 3](#)). AlSiC microprocessor lids are preferred as they meet the demands of



Fig. 2 Heat Sinks in Electronic/Optoelectronic Devices.

light weight, high thermal conductivity, dimensional stability and matching coefficient of thermal expansion with microprocessor assembly (Occhionero and Adams, 2005).

SiC reinforced Aluminum matrix composites are used in carrier/base plate substrates in medical power supply applications and IGBT modules. The traditional power substrate material, copper was replaced by AlSiC composites. The composites offers matching coefficient of thermal expansion which ensures reliability of the device and high thermal conductivity. AlSiC composites also withstand thousands of cyclic thermal stresses without cracking or delamination generated between the dielectric substrates or IC devices (Occhionero *et al.*, 2002). These composites do not require interface layers to get attached to the device substrate and enable direct attachment with substrate materials. This is possible because the coefficient of the thermal expansion of these composites can be adjusted to match with that of the substrate. If the coefficient of thermal expansion of the carrier plates does not match with that of the substrate, then an additional interface layer is required to compensate the thermal stress, which in turn increases the thermal resistance of the system. The fabrication process of this AlSiC is a near net shape process which produces near exact product geometry with threads and holes. This near net shape fabrication provides tight tolerances, cost effectiveness as it delivers high yields, and eliminates costly machining processes. Integration with cooling tubes or very high thermal conductivity insert is possible because of the unique casting processes.

Self-Lubricating Applications of MMCs

To increase the efficiency of the heat dissipation between two relatively moving components and to reduce the energy consumption of such moving parts, new tribological materials have been developed. There have been several strategies to improve the tribological properties of metals. Surface modification, alloying, reinforcements, modification of morphology are some of the strategies to incorporate excellent tribological characteristics in metal. In recent times, self-lubricating reinforcements were developed which removes the needs of external lubricating fluids. Metal matrix composites, fabricated by reinforcing graphite particles, offer self-lubricating property along with excellent wear resistance (refer Fig. 4). They eliminate the requirement of an external lubricant and reduce the coefficient of friction between the moving parts. Graphite is a well-known lubricant and graphite reinforced MMCs offers self-lubricating properties. Such composite systems has the ability to create a thin film of lubricating material, which acts as micro self-lubricating layer. In graphite reinforced MMCs, graphite micro-particles transferred between the contact surfaces function as solid lubricant.

One of the demerits of micron size graphite reinforced aluminum metal matrix composites is that it tend to degrade the mechanical properties. Hardness of graphite reinforced aluminum metal matrix composite has been found to decrease with increase in the graphite content although coefficient of friction and wear rate decrease. Sometimes the mechanical properties of graphite reinforced aluminum matrix composites drop below the mechanical properties of the unreinforced aluminum alloy. This deficiency can be overcome by the development of hybrid composites by adding ceramic particles in graphite reinforced aluminum matrix composites. The hard ceramic particles in this hybrid composite improve its mechanical properties such as hardness whereas the graphite particles in the hybrid composite enhance the self-lubricating properties. Hybrid aluminum matrix composites containing 1 wt% graphite and 10 wt% SiC ceramic particles reduced the wear rate by half that of the wear rate observed in unreinforced aluminum. The mechanical properties of the hybrid Al matrix composites are almost equal to the unreinforced Al alloy. Graphite reinforced Al matrix composites have already been used in automobile cylinder liners due to its self-lubricating properties.

An alternative to the hybrid composite system is composite with single reinforcement, either carbon nano tubes (CNT) or graphene. Graphene and CNT are alternative forms of graphite. Graphene reinforced composites exhibit better mechanical and tribological properties but they post difficulties in fabrication using conventional techniques as well as increase in cost.

Graphite reinforced copper matrix composites show excellent lubrication properties as well as machinability. This type of copper matrix composites replaces lead copper composites, which are banned due to its toxic nature of lead. So lead free copper composite reinforced by graphite has potential to be used in bearing application. The graphite particles in bearing component can be selectively concentrated in the internal periphery to create a graphite rich zone. This creates a surface abundant with graphite particles and the bulk of the component remains unaffected.

Bronze matrix composites reinforced with silver show self-lubricating properties when sliding against stainless steel. These composites were fabricated by powder metallurgy techniques and tested using tribotester in seawater environment. The silver in

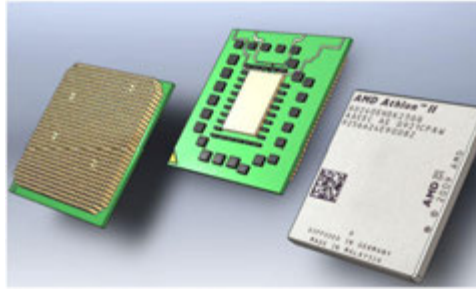


Fig. 3 AMD Athlon II Microprocessor's Substrate & Microprocessor Lid (Adopted from Grabcad.com).



Fig. 4 Graphite plugged bearings and bushings (Adopted from cipcomposites.com).

the composites develops a self-lubricating layer over the worn out surfaces of the composite. Silver reinforcement of about 7 wt% in bronze has exhibited best tribological performance when compared to the monolithic bronze (Cui *et al.*, 2013). Self-lubricating composite coatings on metallic substrate also form the lubricating layer at the surface of the component. Some of the self-lubricating composite coatings developed were $\text{Al}_2\text{O}_3/\text{PTFE}$ (Wang *et al.*, 2010), $\text{NiCr}/\text{Cr}_3\text{C}_2\text{-WS}_2\text{-CaF}_2$ (Liu *et al.*, 2013), WS_2/CaF_2 (Zhang *et al.*, 2009) and MoS_2/Ti (Renevier *et al.*, 2001). These composite coatings eliminate reinforcement dispersion in bulk material and hence such coatings are easier to synthesize.

Self-Healing MMCs

Researchers and engineers are fascinated by the self-healing/self-repairing capabilities of biological systems and efforts are in place to mimic such biological systems. Self-healing is the technique of repairing cracks or damage in the material either autonomously or by influence of external stimulus. These are new class of materials recently developed. Significant successful research efforts in self-healing polymeric materials have been made. In case of metallic materials, due to its low rate of diffusion of metallic atoms and high bond strengths, it is much tougher to heal metals and alloys.

Customized heat treatments, reinforcing shape memory alloys wire and particles in the metal matrix are some of the techniques used to induce self-healing behavior to metal matrix composites. Shape memory alloy (SMA) particles or wires would remember their original shape and return back to their original shape after damage. If a metal matrix composite with SMA particles/wires are cracked, the composite is heated to its austenitic transformation temperature of the shape memory alloys, which alter the SMAs to revert back to its original shape thereby closing the crack formed in the composite.

The healing component of the composite material is generally hypereutectic or hypoeutectic composition. If such a composition is heated to above eutectic temperature, a combination of solid phase and liquid phase in equilibrium will be formed. Thus, the matrix would be molten at the heated temperature. This leads to fusion/welding of the crack during cooling. There is an optimal solid-liquid ratio for effective healing and it was found to be in the range of 20%–30% of the liquid phase. At this optimal solid-liquid ratio, the dendritic structure will be in stable solid state, while the liquid in the interdendritic regions flows freely thus closing the cracks. Self-healing composite materials are developed with Tin based bimetal as matrix and NiTi SMA fibers as reinforcement phase. Self-healing MMC systems have also been developed by embedding microcapsules in metal matrix of high melting temperature. The microcapsules contain a low melting alloy, which will break when cracks get propagated through these microcapsules. The broken microcapsules contained particles of low melting point. If the cracked material is heated until the low melting point material melts, then the melted material flows and fill the developing crack thus closing the crack and arresting the crack propagation (refer Fig. 5). Self-healing MMCs increases the reliability of the part, decreases the maintenance efforts and increases the life of the component.

Electrical Applications of MMCs

Aluminum exhibit higher electrical conductivity with density one third that of copper. Such excellent conductivity combined with lightweight and specific stiffness makes it the best choice for antenna and EMI Shield applications. Graphite fiber reinforced

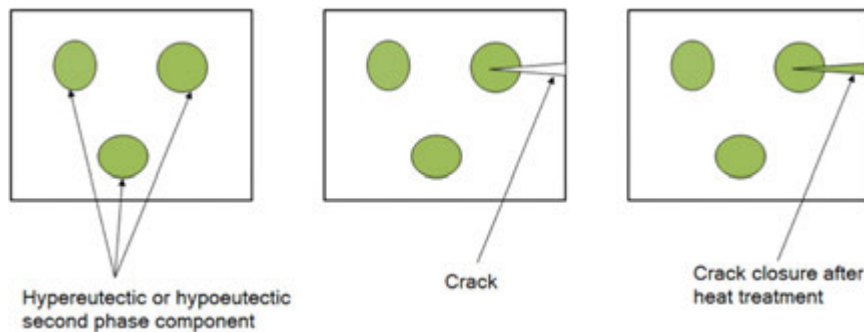


Fig. 5 Mechanism of Crack Closure in Self Healing MMCs.

Aluminum matrix composites exhibit high electric conductance. Its excellent electrical properties made them possible to use in the construction of antenna spar with high gain for Hubble space telescope. This composite is fabricated by reinforcing graphite fibers (P100) in Aluminum alloy matrix (6061) by infiltration process. A preform containing 40% by volume graphite fibers (P100) was used in the infiltration process. This composite also functions as EMI shield (Rawal, 2001). This antenna spar is 3.6 m long and exhibits low coefficient of thermal expansion, which can be used to maintain the position of the antenna during maneuvers in space. This composite also provides electrical signal transmission between the antenna dish and spacecraft.

Magnetic Applications of MMCs

Aluminum is paramagnetic (weakly magnetic) and exhibits insignificant magnetic properties when subjected to intense magnetic field. Its magnetic properties can be improved by reinforcing it with suitable magnetic particles. If the magnetic particles are sufficiently hard, then reinforcing such magnetic particles in aluminum matrix will improve magnetic properties and mechanical properties of the matrix. CoFe_2O_4 nanoparticle is a high coercive magnetic particle, which is known for its magnetic property and its high hardness. It exhibits high chemical stability and moderate magnetic saturation. Magnetomechanical properties of aluminum metal matrix are improved by reinforcing it with this CoFe_2O_4 nanoparticle. These nanoparticles are synthesized sonchemically by reverse method of co-precipitation. The reinforcement of CoFe_2O_4 nanoparticle has led to significant improvement in magnetization value of aluminum metal matrix. The saturation magnetization value of aluminum matrix is 17.07 emu/g with 10 wt% of CoFe_2O_4 nanoparticle (Borgohain *et al.*, 2013). NiFe_2O_4 nanoparticles developed through citrate-nitrate route have been employed to improve the magnetic coercivity and magnetization value of pure aluminum metal (Maleki *et al.*, 2018). NiFe_2O_4 nanoparticles reinforced aluminum matrix composites have significantly improved magnetic properties compared to unreinforced pure aluminum.

Aluminum matrix composite with significant magnetic properties has an advantage over conventional iron based magnetic materials because of its low weight, higher ductility, high specific stiffness, high thermal conductivity and higher ease of manufacturing. Development of magnetic metal matrix composites with good magnetic properties without compromising the mechanical properties or with improvement of mechanical properties open new avenues of application of such composites. Engineering applications of magnetic metal matrix composites are development of sensitive measuring devices and novel fuel-efficient engineering devices for automobiles, ships and aircrafts.

Future Prospects and Challenges

The exploration of the novel non-structural applications of metal matrix composites has started recently by researchers and engineers. It is expected that the applications of metal matrix composites will grow enormously with customization of metal matrix composites to specific industries. With development of additive manufacturing, the fabrication process of these composites is expected to change in coming years.

Novel self-lubricating Aluminum matrix composites exhibit potential to mitigate fretting wear in mechanical assemblies encountering fretting motion. Fretting loading is a wear mechanism that occurs in a small amplitude oscillatory and/or radial relative motions between two contacting components in an assembly (Ali *et al.*, 2010, 2009). Fretting contact may combine with fatigue loading in assemblies where vibrations are dominant resulting in fretting fatigue (Ali and Raman, 2010). Nano silver particles can be reinforced in aluminum alloy to fabricate aluminum matrix composites with self-lubrication characteristics to be used in fretting wear situations. Silver particles may form a debris bed (third body) which reduce the fretting wear rate and cracking. Graphite and SiC reinforced aluminum also show potential to be used in aeronautical applications where self-lubrication can be used to resist fretting loading.

Other potential non-structural applications of MMCs are in electronic detectors in MRI/NMRI systems and in CT scanners.

MMCs have been investigated for its potential application in high precision space optics. Plasma thermal sprayed ceramic particle reinforced Al matrix composites (Jiang and Nikanpour (2000)), graphite-cyanate composites (Ozaki *et al.*, 1996), hybrid

carbon fiber reinforced SiC composites (Krödel and Tsuyoshi, 2007) have been evaluated for space mirrors and space optical telescopes. Future space optical mirrors and optical telescopes are expected to be these metal matrix composites.

Other challenges that affect the future applications of MMCs include,

- (1) Development of MMCs with higher ductility and fracture toughness
- (2) Understanding of microstructural development in MMCs
- (3) Need of reliable and low cost non-destructive inspection methods for MMCs
- (4) Developments of low cost and high quality reinforcements for MMCs
- (5) Development of reuse/recycling techniques for MMCs
- (6) Development of low cost secondary processing techniques for MMCs

References

- Ali, M., Joshi, S.C., Sultan, M.T.H., 2017. Palliatives for low velocity impact damage in composite laminates. *Advances in Materials Science and Engineering*. 1–16. 8761479.
- Ali, M.M., Raman, S.G.S., 2010. Effect of plasma nitriding environment and time on plain fatigue and fretting fatigue behavior of Ti–6Al–4V. *Tribology Letters* 38, 291–299.
- Ali, M.M., Raman, S.G.S., Pathak, S., Gnanamoorthy, R., 2009. Fretting wear behaviour of plasma nitrided Ti–6Al–4V fretted against unnitrided Ti–6Al–4V and alumina counterbodies. *Transactions of the Indian Institute of Metals* 62, 59–64.
- Ali, M.M., Raman, S.G.S., Pathak, S., Gnanamoorthy, R., 2010. Influence of plasma nitriding on fretting wear behaviour of Ti–6Al–4V. *Tribology International* 43, 152–160.
- Borghain, C., Acharyya, K., Sarma, S., *et al.*, 2013. A new aluminum-based metal matrix composite reinforced with cobalt ferrite magnetic nanoparticle. *Journal of Materials Science* 48, 162–171. <https://doi.org/10.1007/s10853-012-6724-4>.
- Cui, G., Bi, Q., Yang, J., Liu, W., 2013. The bronze–silver self-lubricating composite under sea water condition. *Tribology International* 60, 83–92. <https://doi.org/10.1016/j.triboint.2012.11.006>.
- Jiang, X.-X., Nikanpour, D., 2000. Characterization of aluminum metal-matrix composite (MMC) for lightweight space optics application: A study of thermal expansion behavior of MMC in simulated space thermal environment. Presented at the Proceedings of SPIE.
- Krödel, M.R., Ozaki, T., 2007. HB-Cesic composite for space optics and structures. Presented at the Proceedings of SPIE.
- Liu, X.-B., Liu, H.-Q., Liu, Y.-F., *et al.*, 2013. Effects of temperature and normal load on tribological behavior of nickel-based high temperature self-lubricating wear-resistant composite coating. *Composites Part B: Engineering* 53, 347–354. <https://doi.org/10.1016/j.compositesb.2013.05.032>.
- Occhionero, M.A., Adams, R.W., 2005. AlSiC, and AlSiC hybrid composites for flip chips, optoelectronics, power, and high brightness LED thermal management solutions. Presented at the 2005 6th International Conference on Electronic Packaging Technology, pp. 1–5. Available at: <https://doi.org/10.1109/ICEPT.2005.1564720>.
- Maleki, A., Taherizadeh, A.R., Issa, H.K., *et al.*, 2018. Development of a new magnetic aluminum matrix nanocomposite. *Ceramics International* 44, 15079–15085. <https://doi.org/10.1016/j.ceramint.2018.05.141>.
- Occhionero, M., Fennessy, K., Adams, R., Sundberg, G., 2002. AlSiC baseplates for power IGBT modules: Design, performance and reliability. Presented at the IMAPS New England Symposium.
- Ozaki, T., Ikeda, C., Isoda, M., Tsuneta, S., 1996. New high-thermal-conductivity composite material for high-precision space optics. Presented at the Proceedings of SPIE.
- QU, X., ZHANG, L., WU, M., REN, S., 2011. Review of metal matrix composites with high thermal conductivity for thermal management applications. *Progress in Natural Science: Materials International* 21, 189–197. [https://doi.org/10.1016/S1002-0071\(12\)60029-X](https://doi.org/10.1016/S1002-0071(12)60029-X).
- Rawal, S., 2001. Metal-matrix composites for space applications. *Journal of the Minerals Metals & Materials Society* 53, 14–17.
- Renevier, N.M., Hampshire, J., Fox, V.C., *et al.*, 2001. Advantages of using self-lubricating, hard, wear-resistant MoS₂-based coatings. *Surface and Coatings Technology*, Proceedings of the 7th International Conference on Plasma Surface Engineering, vol. 142–144, pp. 67–77. Available at: [https://doi.org/10.1016/S0257-8972\(01\)01108-2](https://doi.org/10.1016/S0257-8972(01)01108-2).
- Sanjay, K., Maurya, S.P., Akansha, D., Md, Thariq, Imteyaz, A., 2019. Cu–Ba_{0.7}Si_{0.3}TiO₃ composites for electronic packaging. *Journal of Materials Science: Materials in Electronics* 30 (9), 1–7.
- Sarno, C., 2001. Thermal management of highly integrated electronic packages in avionics applications. *Electronic Cooling*. Available at: <https://www.electronics-cooling.com/2001/11/thermal-management-of-highly-integrated-electronic-packages-in-avionics-applications/>.
- Wang, Z., Wu, L., Qi, Y., Cai, W., Jiang, Z., 2010. Self-lubricating Al₂O₃/PTFE composite coating formation on surface of aluminium alloy. *Surface and Coatings Technology* 204, 3315–3318. <https://doi.org/10.1016/j.surfcoat.2010.03.049>.
- Yoshida, K., Morigami, H., 2004. Thermal properties of diamond/copper composite material. *Microelectronics Reliability* 44, 303–308. [https://doi.org/10.1016/S0026-2714\(03\)00215-4](https://doi.org/10.1016/S0026-2714(03)00215-4).
- Zhang, X.-F., Zhang, X.-L., Wang, A., Huang, Z., 2009. Microstructure and properties of HVOF sprayed Ni-based submicron WS₂/CaF₂ self-lubricating composite coating. *Transactions of Nonferrous Metals Society of China* 19, 85–92. [https://doi.org/10.1016/S1003-6326\(08\)60233-2](https://doi.org/10.1016/S1003-6326(08)60233-2).
- Zweben, C., 1992. Metal-matrix composites for electronic packaging. *The Journal of the Minerals, Metals & Materials Society* 44, 15–23.
- Zweben, C., 2005. Ultrahigh-thermal-conductivity packaging materials. Presented at the Semiconductor Thermal Measurement and Management IEEE Twenty First Annual IEEE Symposium, pp. 168–174. Available at: <https://doi.org/10.1109/STHERM.2005.1412174>.

Relevant Websites

- <https://www.mensjournal.com/adventure/surfboard-technology-from-outer-space/>
Men's Journal.
- <https://www.idtechex.com/en/research-article/metal-matrix-composites-mmc-finally-reaching-the-top-of-wish-lists/13709>
Metal Matrix Composites (MMC): Finally reaching the top of wish lists.
- <https://www.sciencedirect.com/topics/materials-science/metal-matrix-composite>
Metal Matrix Composite.
- <https://www.astbearings.com/metallic-self-lubricating-bushings.html>
Metallic Self-Lubricating Bushings.
- <https://materion.com/products/metal-matrix-composites/supremex/space-defense-and-optical-systems>
SupremEX Metal Matrix Composites (MMCs)
Materion.

Introduction: Polymer Matrix Composite Materials

Dermot Brabazon, I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin, Ireland

© 2021 Elsevier Inc. All rights reserved.

Particulate Reinforced Polymer Matrix Composites

There are a wide variety of materials, structures and routes for the production of polymer composite materials ([Singh et al., 2021](#)). Particulate is a very common structure of reinforcement utilized within polymer matrix composites. There are many forms of particulate morphology and material type. In recent times, there has been a focus on the introduction of particulate reinforcement within polymers that are additively manufactured, either within the feedstock preparation or during the feedstock deposition. As example of ABS filaments to be used for Fused Deposition Modeling with graphene reinforcement was presented in the work of [Singh and Kumar \(2021\)](#). The exfoliated graphene was mixed with ABS before extrusion into the reinforced filament which resulted in a filament with much great thermal conductivity of 7.6 W/mK. Higher mechanical properties are often sought from polymer matrix composites than can be achieved from the matrix material alone.

Fiber Reinforced Polymer Matrix Composites

Fiber reinforced polymer matrix composites are in particular used where very demanding physical properties are required. E-glass, S-glass, carbon, aramid and boron fiber are common fiber reinforcements and can be integrated within the polymer composite in many ways. One common method for composite fiber direction control is achieved through the use of laminated polymer composites. The range of polymer composite matrix and reinforcements as well as the effect of fiber orientation is presented by [Ghamarian et al. \(2021\)](#). In addition to traditional thermosets and thermoplastic polymers, rubber materials are also reinforced with particulate and fiber reinforcements. In the article from Irez et al., the reinforcement of epoxy-rubber with alumina fiber and boron nitride particulate was examined ([Irez et al., 2021](#)). The ability to produce such reinforced rubber materials could provide a long life and reuse of materials, providing at more environmentally friendly life cycle.

Biomedical Applications of Polymer Matrix Composites

The production of bone PMMA cements with various reinforcing agents is an area where there has been a lot of published research. Thermal, mechanical and biological properties are important considerations for such materials. Reinforcing agents include hydroxyapatite, carbon based nanomaterials, and chitosan. A review of the research in this area and resulting physical properties is presented in the article of [Bakhtiari et al. \(2021\)](#).

A detailed review of biopolymers matrix composites for medical applications is presented in the article of [Shariatnia \(2021\)](#). A range of biopolymers and their applications are presented. These include chitosan, carboxymethyl chitosan, alginate, hyaluronic acid, cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, chondroitin sulfate, starch, carboxymethyl starch, zein, gelatin, gellan gum, acacia gum, guar gum, tamarind gum, xanthan gum composites, pectin, collagen and polyhydroxy butyrate composites. The biological and environmental advantages of these biopolymers over conventional fossil fuel based polymer composites are discussed in this article.

Hydrogel films are three dimensional crosslinked hydrophilic polymers which can absorb large amount of water without solubilizing or losing integrity due to their strong internal bonds. This allows them to be applied for wound healing. Hydrogel composites can be reinforced with biopolymers such as polysaccharides, proteins and peptides, natural gums, or synthetic polymers such as PVA, PVP, or non-organic materials as discussed by [Khan et al. \(2021\)](#).

A significant amount of research internationally is examining polymer matrix composites for organ reconstruction ([Syed et al., 2021](#)). In this work, thermoplastic, thermosets, elastomers, and resorbable polymers are used. Reinforcing elements include natural and synthetic fibers, which more common implants include bone, joints, and dental scaffolds.

Other Application Areas for Polymer Matrix Composites

Polymer matrix composites are used in water filtration applications. In the article from Ahmadzadeh and Mohammadi, carbon nanotubes (CNTs) and graphene oxide (GO) are discussed in terms of their ability to improve the adsorption capacity as well as mechanical, chemical and thermal resistance of the polymer composite ([Tofghy and Mohammadi, 2021](#)). Recent developments in water and wastewater treatment applications are reviewed in their article.

Another large sector area where polymer matrix composites are used is in the aerospace industry. In this case, high specific strength, good fracture resistance, and high damage thresholds are generally sought. The percentage of fiber reinforced polymers

used in the aerospace industry has been increasing in recent years due to their superior properties. Devaraju and Alagar present a detailed review of the latest developments in this area (Devaraju and Alagar, 2021).

New Materials and Processing Methods for Polymer Matrix Composites

As for the other composite materials, additive manufacturing has been applied increasingly in recent years for the manufacture of polymer matrix composites. The developments in this area is presented in detail by Bahksheshi *et al.* (2021). Methods presented include SLS, stereolithography, direct ink writing, binder jetting, and fused filament fabrication. Both natural and synthetic materials as applied to polymer matrix composite production via additive manufacturing and related applications are presented.

A range of new polymers and their applications is presented in the article by Liu (2021). Some unique discussion in this article includes that on the shape memory and self-healing materials, as well as the composite applications in electrochemical and gas barrier membranes.

The notion of a multi-functional polymer matrix composite is important in general for composite materials. Through this, it is meant that the reinforcing phase and matrix are stable well bound together, can act as a unique multi-purpose material, and can exhibit properties under different external stimuli (Mhaske *et al.*, 2021; Nyabadza *et al.*, 2021). Some examples of multi-functional composites are presented in this review including in applications of smart packaging, self-healing, drug delivery, batteries and sensing.

References

- Bahksheshi, R., Pahlevanzadeh, F., *et al.*, 2021. Additive manufacturing of polymer matrix composites. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 1013–1028.
- Bakhtiari, S.S.E., *et al.*, 2021. Poly(methyl methacrylate)-based composite bone cements with different types of reinforcement agents. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 867–886.
- Devaraju, S., Alagar, M., 2021. Polymer matrix composite materials for aerospace applications. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 947–969.
- Ghamarian, N., *et al.*, 2021. Effect of fiber orientation on the mechanical properties of laminated polymer composites. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 746–765.
- Irez, A.B., *et al.*, 2021. A new design of epoxy based composites reinforced with devulcanized rubber, alumina fiber and BN. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 1069–1080.
- Khan, I.U., *et al.*, 2021. Hydrogel composite films for wound healing. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 887–904.
- Liu, P., 2021. New design consideration of polymer matrix composite materials. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 1029–1037.
- Mhaske, S.T., *et al.*, 2021. Preparation and applications of synergically combined polymer matrix composites. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 1112–1134.
- Nyabadza, A., Kane, J., Vázquez, M., Sreenilayam, S., Brabazon, D., 2021. Multi-Material Production of 4D Shape Memory Polymer Composites. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. <https://doi.org/10.1016/B978-0-12-819724-0.00057-4>. vol. 2, pp. 879–893.
- Shariatnia, Z., 2021. Biopolymer matrix composites for new medical applications. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 842–866.
- Singh, J., *et al.*, 2021. Processing of polymers and their composites: A review. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 2, pp. 577–603.
- Singh, R., Kumar, R., 2021. Development of low-cost graphene-polymer blended in-house filament for fused deposition modeling. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 1081–1090.
- Syed, H.K., *et al.*, 2021. Polymer composites for organ reconstruction. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 905–914.
- Tofighy, M.A., Mohammadi, T., 2021. Polymer matrix composites materials for water and wastewater treatment applications. In: Brabazon, D. (Ed.), *Encyclopedia of Materials: Composites*. Oxford: Elsevier. vol. 1, pp. 983–997.

Overview of Mechanical and Physicochemical Properties of Polymer Matrix Composites

Kai Bin Liew, University of Cyberjaya, Cyberjaya, Selangor, Malaysia

Choon Fu Goh, Universiti Sains Malaysia, Penang, Malaysia

Sajid Asghar and Haroon K Syed, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

© 2021 Elsevier Inc. All rights reserved.

Introduction

Over the past decade, there was a surge of needs in the manufacturing industries for materials with an enhanced performance for enhanced tensile strength, stiffness, density and functionality. On top of that, such materials should not incur a high production cost with greater sustainability initiatives.

Conventional materials such as metal with a single element has limited applications. Polymer is, thus, a preferred alternative. More recently, polymer composite materials are named as one of the alternatives with enhanced properties ([Yashas Gowda *et al.*, 2018](#)). Polymer matrix composites (PMC) have two major phases – continuous phase and dispersed phase. The continuous phase consists of different types of organic polymers that serve as the matrix to bind the dispersed phase, usually reinforcing fibers, together for an efficient transfer of load between them. The matrix is important as it serves as a platform to distribute the fibers evenly throughout the structure. Therefore, the properties of PMC depend on the matrix, reinforcement and the interphase. The reinforcing fibers enable the enhanced properties such as fracture toughness, tensile strength and stiffness. PMCs may also show added advantages of ease of processing, lightweight, higher productivity, and in cost reduction. Different types of fillers and fibers can be incorporated into the polymer matrix to achieve different applications ([Cao *et al.*, 2008](#)).

The mechanical and physicochemical properties of PMC are affected by mainly but not limited to the types and relative proportions of matrix and reinforcement, the geometry of the reinforcement, and the nature of the interphase. In this article, we will first discuss the mechanical and physicochemical properties of PMC in general, following by a brief discussion of mechanical and physicochemical properties by types of PMC.

General Mechanical Properties of PMC

High Specific Strength and Specific Modulus

In general, PMC have improved specific strength and specific modulus compared to the conventional polymer. The specific strength is the ratio of strength and density while the specific modulus is the ratio of modulus and density, and the dimensions or units are both length. These parameters also explain the bearing capacity and stiffness properties of a material with a fixed weight. Materials with high specific strength and specific modulus are desired in many critical industries such as aerospace and construction. The comparisons of specific strength and modulus of several PMC with conventional materials such as steel and alloys are presented in [Table 1](#).

Composite materials with a high specific strength and specific modulus are often a result of the high-performance and low-density of reinforcing fibers. Therefore, it is not surprised to have carbon fiber/epoxy composites showing the highest specific strength and modulus.

Good Fatigue Resistance and High Damage Tolerance

Metallic materials with a moderate fatigue failure crack easily when a high load is applied. A strong adherence at the interface between fiber and matrix play an important role here to prevent crack of the PMC. The cracks in a material normally starts from the weak link of fibers and the damage continue to deepen before the final destruction is achieved. Carbon fiber matrix composite usually has a stronger fatigue resistance as compared to wood epoxy laminates and glass fiber polymer-matrix composites. The fatigue strength of conventional metallic materials the majority of materials lies between 30%–50% of tensile strength whereas the fatigue strength of carbon fiber composite material is typically higher recorded at 70%–80% of tensile strength. As a result, the propagation of cracks in PMC is slower compared to conventional metallic materials. This is then followed by a series of damaging events such as matrix cracking, interfacial debonding, fiber pull-out and fiber split or break before leading to the final destruction. When a small number of fibers fracture, the part of the load can be transferred via the matrix to the other fibers. This characteristic makes PMC more robust and not fracture easily within a short period. The fatigue resistance of a composite material depends on various factors such as the fiber lay-up configuration, geometry of the structure and temperature ([Tomioka *et al.*, 2011](#)).

Table 1 Specific strength and specific modulus of commonly used materials and PMC fiber composites

Materials	Density (g/cm ³)	Tensile strength (GPa)	Elastic modulus (10 ² GPa)	Specific strength (10 ⁶ cm)	Specific modulus (10 ⁸ cm)
Steel	7.80	1.03	2.10	1.30	2.70
Aluminum alloy	2.80	0.47	0.75	1.70	2.60
Titanium alloy	4.50	0.96	1.14	2.10	2.50
Glass fiber composite materials	2.00	1.06	0.40	5.30	2.00
Carbon fiber II/epoxy composite materials	1.45	1.50	1.40	10.30	9.70
Carbon fiber I/epoxy composite materials	1.60	1.07	2.40	6.70	15.00
Organic fiber/epoxy composites	1.40	1.40	0.80	1.00	5.70
Boron fiber/epoxy composites	2.10	1.38	2.10	6.60	10.00
Boron fiber/aluminum matrix composites	2.65	1.00	2.0	3.80	7.50

Note: Adopted from Wang, R.M., Zheng, S.R., Zheng, Y.P., 2011. *Polymer Matrix Composites and Technology*. Netherlands: Elsevier. (Woodhead Publishing Series in Composites Science and Engineering).

Good Damping Characteristics

Some materials such as rubber and polymers are well known of their viscoelastic behavior due to the molecular structure of the polymer chains. The shortfalls of these materials are the lack of stiffness and a low vibration damping. Normally, the viscous behavior of rubber and polymers is generally temperature dependant. The viscous behavior of these materials is particularly strong over a narrow temperature around the glass transition temperature. In contrast, the viscous behavior of PMC with ceramic and carbon is prominent over a wide temperature range. This property renders PMC to be a more stable alternative.

The matrix contributes to the viscous behavior of PMC while the fibers are responsible for the elasticity of PMC. An increased fiber volume fraction enhances the elasticity parameters such as storage modulus and loss modulus but decreases the loss tangent which indicates the viscous characteristic (Chua *et al.*, 2015). PMC also have a high natural frequency and low resonance due to the ability of the interface between the fiber and matrix to absorb vibrational energy. Hence, the structure of PMC can stop vibration in a short period of time when it happens. As a result, this characteristic of resistant to vibration contributes to a tough and solid structure of PMC which allows PMC to be applied in much wider fields.

High Instantaneous Temperature Resistance

Some PMC such as fiberfill reinforced plastic (FRP) has a high thermal resistance. The thermal conductivity of this PMC is reported to be only 1% of metal materials. Due to this reason, FRP can be applied in an area that requires materials with a high specific heat, melting heat and vaporization heat such as protective materials for a missile nose cone.

Superior Electric Insulation Performance

Beside thermal resistance, FRP also shows a good electric insulation property which can be used as high-frequency wave-transparent materials for a radome.

Good Friction Property

Carbon fibers have low friction coefficient and self-lubricating properties. Therefore, the related composite materials have good friction-resistance and antifriction properties.

Static Mechanical Property

Mechanical properties of PMC can be enhanced by increasing the continuous carbon fiber volume within the PMC. However, an excessive addition of continuous carbon fibers may reduce the mechanical properties due to an inadequate binding of the fibers by the polymer matrix when exceeding the maximum interface bonding capacity. He and Gao (2015) reported that when the continuous carbon fiber volume increases from 50 to 70 vol% in an epoxy based polymer matrix, the flexural properties of the PMC were enhanced. However, the flexural properties reduce when the continuous carbon fiber volume increases above 70 vol%.

The addition of discontinuous short carbon fibers to a polymer matrix increases the tensile modulus of the PMC provided that a strong fiber-matrix bonding is established. The addition of discontinuous short carbon fibers up to 10 wt% to poly (trimethylene terephthalate) was shown to increase the tensile strength of the PMC. Similar observation was obtained when discontinuous short carbon fibers were added to the thermoplastic liquid crystal copolymer that increases both tensile strength and modulus due to a

good bonding between matrix and fiber interface. Carbon fibers showed a more significant increase in tensile strength compared to synthetic graphite powders due to a different bonding strength (Keith *et al.*, 2007). On the other hand, the addition of discontinuous short carbon fibers to polyvinylidene fluoride decreases the tensile strength and ductility due to the poor bonding between fiber and matrix (Ram *et al.*, 2014).

The adherence between matrix and fiber does not just depend on the affinity of the fiber. The matrix plays an important role. For example, epoxy is known as an excellent adhesive that provide many adhesive sites for fibers to attach at. Fibers with oxygen functional group can easily react with epoxy to form bonds (Semoto *et al.*, 2013).

Mohanty and Srivastava (2015) has conducted a study to compare the impact of addition of short carbon fibers and short glass fibers to epoxy on the mechanical properties of the PMC formed. It was reported that short carbon fibers were more effective to enhance the mechanical properties of PMC than short glass fiber in terms of flexural strength, flexural modulus and Charpy impact energy. Dang *et al.* (2012) has investigated the effect of addition of copper-coated carbon fibers to epoxy. It was reported that the tensile strength and modulus increases with an increase of filler content up to 0.5 wt%. The mechanical properties were weakening with increasing filler content above the optimum value.

Song *et al.* (2016) has reported a study on addition of short carbon fibers to acrylonitrile-styrene-acrylate copolymer. The addition of the filler caused increase in tensile strength and flexural modulus with increasing of filler amount. The flexural strength and the flexural modulus have increased by a percentage of 122% and 464% respectively at 30 wt% carbon fibers addition. Geng *et al.* (2007) has studied the addition of silica nanoparticle (20 nm diameter at 10 wt%) to a short carbon fiber-bismaleimide matrix composite. The flexural strength, tensile strength, flexural modulus and tensile modulus have increased by a percentage of 12%, 6%, 5% and 11% respectively. On top of that, the storage modulus, loss tangent and glass transition temperature T_g have also reported an increase in value.

Carbon nanotube and carbon nanofiber (CNT/CNF) have also been used as reinforced fibers for polymers. CNT and CNF have good binding capability with polymer. The higher the amount of multi walled CNT (MWCNT), the higher the increase in tensile strength and tensile modulus of epoxy based matrix. The incorporation of MWCNT (10–25 nm diameter, 5–10 μm long, 0.3 vol%) to epoxy increases the tensile strength and compressive strength, interfacial shear strength (IFSS) for the interface between carbon fiber and epoxy (Wang and Li, 2016). Double walled CNT (DWCNT) have also been used to increase the fracture toughness of epoxy. Gojny *et al.* (2004) has incorporated amino-functionalized DWCNT (2.8-nm diameter, 0.1 wt%) to epoxy based polymer and the fracture toughness increases from 0.65 to 0.77 MPa but the effect on tensile strength and modulus is weak.

Subramaniam *et al.* (2016) has reported a study of using combination of short chain fibers and MWCNT as reinforced fibers in epoxy based matrix. The combination has recorded synergistic effect in relation to the tensile strength, fracture toughness, and impact strength. The synergistic effect is postulated as a result of the ability of MWCNT to promote plastic deformation of the epoxy matrix and decrease the stress concentration near the interface between the short carbon fibers and the epoxy matrix.

Carbon black can also be used as reinforced fiber in PMC. Carbon black (2–20 nm) has shown better results than MWCNT to enhance the tensile strength and ductility of a styrene butadiene matrix composite. In the study conducted by Tabačiarová *et al.* (2016), carbon black showed an increase in tensile strength by 1205% whereas MWCNT has increased tensile strength by 310%. On the other hand, carbon black has increased the tensile ductility from 300% to 860% but MWCNT has decreased the tensile ductility from 300% to 230%.

Environmental Degradation

Environmental degradation due to moisture, heat and ultraviolet is an important criteria of consideration for PMC used in critical industries. Carbon fiber enhanced epoxy matrix composite degrades under a normal hygrothermal pressure that results in a significant reduction of mechanical strength (Larbi *et al.*, 2015). The epoxy matrix can absorb moisture leading to an increased in the PMC volume and the contact electrical resistivity of the interlaminar interface of the laminate.

On the other hand, thermoplastic polymer based PMC are more resistant to moisture. The major disadvantage of this PMC is the UV degradation. Poly(ether-ketone-ketone) (PEKK) based PMC is a common example due to its high glass transition temperature, strong mechanical strength and fracture toughness, low moisture absorption and good environmental resistance. However, UV might accelerate weathering condition (Mazur *et al.*, 2014).

Recovery and Recycling of Fibers

Environmental friendly materials are desired in industry. Carbon fibers in the PMC can be recycled from cured or uncured scraps of epoxy-matrix composites by pyrolysis, followed by oxidative removal of any organic residual. The recovered fibers show similar properties to pure fibers.

On the other hand, there are also thermosetting matrices which cannot be recovered and recycled. These matrices have little value of reuse after cured. The process to recycle these PMC is tedious and it is unpractical economically. Researches have also been done on the reuse of scrap form of PMC. The scrap form of thermosetting PMC is found with little economical value. However, PMC with thermoplastic characteristics can be used in scrap form (Giorgini *et al.*, 2015).

Physicochemical Properties and Characterization Method of PMC

Infrared (IR) Spectroscopy Analysis

Infrared (IR) spectroscopy has gained widespread use as a crucial analytical technique to characterize PMC. The near IR region $4000\text{--}400\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) is useful for applications in characterizing PMC. Spectra formation relies on the IR radiation absorption that gives rise to the molecular stretching and bending vibrations. Within the near IR region, there exists a fingerprint region ($1800\text{--}400\text{ cm}^{-1}$) containing multiple peaks of narrow line width but remains a strong identity for differentiation of molecular interactions. Fourier transform (FT) spectrometers is an instrumentation that allows a stronger signal-to-noise, rapid spectral acquisition and a better resolution than a typical dispersive spectrometer. The FT instrumentation can be found frequently to be combined with a technique called attenuated total reflection (ATR) spectrometry where multiple internal reflections can occur at the interface between the sample and ATR crystals of high refractive index (such as zinc selenide, germanium and diamond). This technique also generates an evanescent wave which allows the penetration of the IR beam into the sample and this shows an excellent signal-to-noise ratio. Moreover, this analysis requires very minimum or no sample preparation but good contact is required between the sample and the ATR crystal. Eibl (2017) compared bench-top and hand held IR spectrometers as well as ATR and diffuse reflectance (DR) methods in the investigation of thermal damage on the epoxy matrix with carbon fibers. The results from bench-top and hand held IR spectrometers are comparable. But DR methods are preferred for bulk material owing to the difficulty in predicting the duration and temperature of the thermal pre-load for the bulk ATR method.

FTIR spectroscopy is a non-invasive technique that identifies the components in PMC and measures interactions between the components. This analysis was utilized by Cecen *et al.* (2008) in showing the interaction between reinforcing fibers in epoxy- and polyester-based composites synthesized via solution method using vacuum-assisted resin transfer molding (VARTM). An interaction between fibers and resin was seen due to the shift of OH stretching vibrations of epoxy (3364 cm^{-1}) and polyester (3448 cm^{-1}) to a lower wavenumber. With an additional new band at 2360 cm^{-1} for carbon/epoxy composites, it was shown that the interaction between carbon fiber and epoxy resin is stronger than the counterparts with glass fibers. Reinforcement of composites comprising of polylactic acid (PLA), sisal fibers (SF) and a commercial grade epoxy-functionalized oligomer Joncryl ADR[®]-4368 (ADR) by the addition of poly (butylene-adipate-terephthalate) (PBAT) resin was noted with an increased intensity of C = O stretching vibrations (1735 cm^{-1}) (Wu and Hao, 2019). FTIR analysis in different spectral ranges was followed by Agrebi *et al.* (2019) to understand the degree of reinforcement of a nanocomposite of natural rubber by the addition of cellulose nanoparticles. Apart from identifying molecular interactions of added materials into PMC, FTIR analysis was demonstrated by Tonetto *et al.* (2013) to confirm the conversion of resin cements, a dental PMC, under light curing. The C = C stretching vibrations (1638 cm^{-1}) were monitored in relative to the aromatic C–C (1608 cm^{-1}) before and after the curing process. In addition, FTIR spectroscopy was used to perform surface characterization of silanised lignocellulose fibers reinforced with epoxidised natural rubber/poly-lactide (ENR/PLA) composites (Masek *et al.*, 2016). The intensity of epoxide groups (C–O–C) of ENR at 1248 and 880 cm^{-1} was greatly reduced indicating the reaction of oxirane ring of ENR with amine group of silane from silanised lignocellulose fibers.

Chemometric analysis such as principal component regression (PCR) and related technique, principal component analysis (PCA) can be applied to identify subtle changes in large datasets of IR spectra. The use of multivariate data analysis in deconvoluting FTIR data has been applied to investigate thermal degradation or incipient thermal damage of PMC such as carbon fiber reinforced bismaleimide resins (Toivola *et al.*, 2018) and carbon fiber reinforced epoxy system including HexPly[®] 8552/IM7 and HexPly[®] M18-1/G939 (Eibl, 2017; Eibl and Wolfrum, 2012; Wolfrum *et al.*, 2016). Particularly, this spectral analysis provides an accurate estimation for the duration and temperature of a thermal pre-load for PMC. Toivola *et al.* (2018) achieved the differentiation of the interlaminar shear strength (ILSS) carbon fiber-bismaleimide composites over a temperature range by using multivariate analysis of the first derivative of absorbance spectra (Fig. 1). It is well recognized that the differences in the IR diffuse reflectance spectra of the samples are hardly identified after thermal exposure at different temperatures (Fig. 1(a)). The first three principal components explained more than 95% of the total variation in the spectra (Fig. 2). The regression coefficients (RCs) were used by the model to relate the identified principal components of the ILSS of the composites. Several peaks reported in the first principal components including 1188 , 1374 , 1556 , and 1712 cm^{-1} are associated with functional groups that participate in important thermal exposure reactions. The correlation between PCR calibration model and the ILSS of the samples shows an excellent linear regression (Fig. 3(a)). The horizontal dashed line in Fig. 3(b) indicates that this model predicts statistically significant differences in ILSS after 232°C exposure. Comparing to the physical damage evaluated by ultrasonic testing (UT), the vertical dashed line shows that the detection threshold of physical damage happens between 316 and 330°C . The model used can improve the detection of ILSS loss (chemical damage) by more than 75°C as compared with UT. This also explains that thermal damage causes the loss of $\sim 50\%$ of the original ILSS which is not detected previously by UT.

Morphological Properties by Scanning Electron Microscopy

Microscopy, usually minimally or non-destructive, provides a rapid analysis of a small amount of sample for morphologic properties including size and shape. Owing to a higher magnification and resolution than normal light microscope, scanning electron microscopy (SEM) is a frequently used morphological analysis method that employs the scanning with an electron beam. For samples that are not electrically conductive, a thin coating of metal such as gold or platinum is applied. SEM results are supportive evidences to the findings from other analyses such as mechanical test and FTIR spectroscopy.

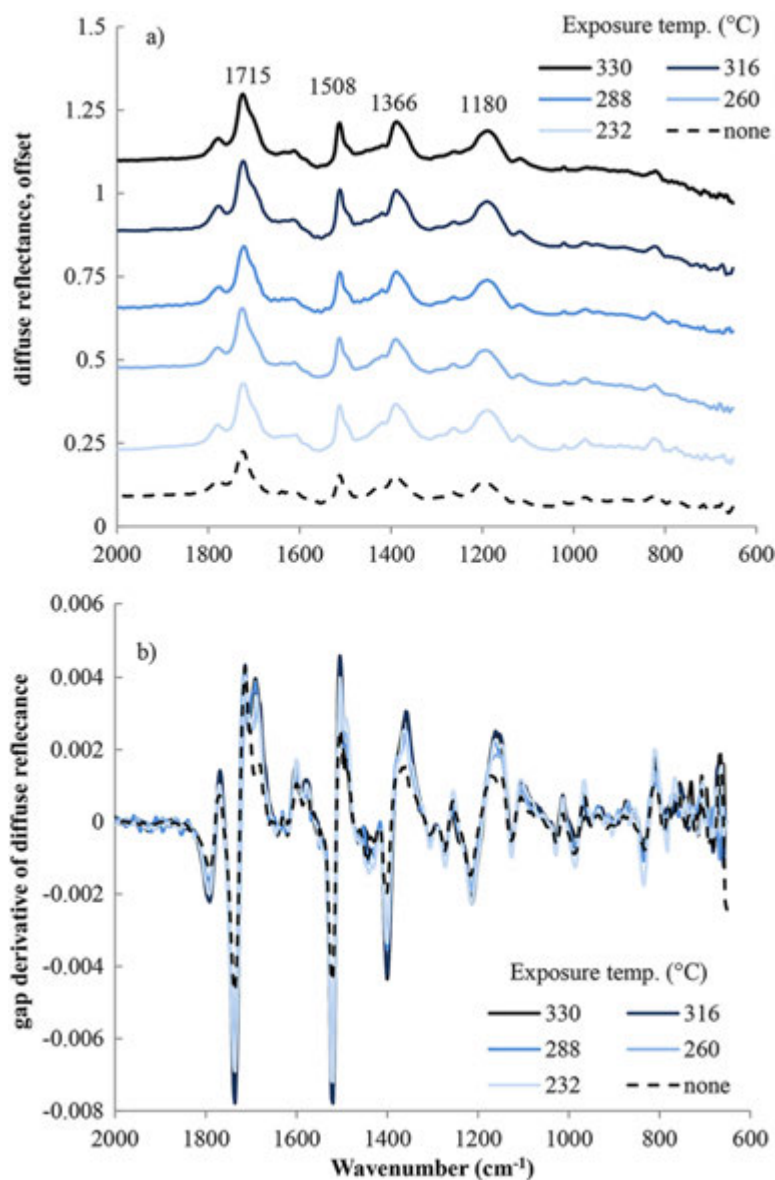


Fig. 1 (a) IR diffuse reflectance spectra for carbon fiber-bismaleimide resin laminate ILSS samples after thermal exposures. (b) Gap 1st derivative of IR diffuse reflectance spectra after thermal exposures. Adapted from Toivola, R., Afkhami, F., Baker, S., McClure, J., Flinn, B.D., 2018. Detection of incipient thermal damage in carbon fiber-bismaleimide composites using hand-held FTIR. *Polymer Testing* 69, 490–498.

SEM is commonly used to observe distribution of reinforcing materials in PMC. Yunus and Alsoufi (2018) observed a homogeneous distribution of bioceramic fillers such as titanium oxide (TiO₂) and alumina (Al₂O₃) in the hybrid polymer matrix composites with high-density polyethylene (HDPE) with SEM image analysis. Apart from analysing the distribution of reinforcing materials in the matrix, SEM has also been used to examine interfacial failure or adhesion of PMC during fracture. Considering that added fibers are tightly connected with the matrix or underlain the matrix, they tend to be broken and torn up in the composites. Cecen *et al.* (2008) reported that poor fiber/matrix adhesion is observed in polyester composites with carbon and glass fiber due to extensive damage. The clean fiber surfaces on epoxy-based composite reinforced with glass fiber reflect extensive interfacial failure. The fibers are loosely held by the matrix material after failure. However, epoxy composites demonstrated considerable matrix failure together with the carbon fibers, indicating a good interfacial adhesion. In recent study by Latief *et al.* (2019), the addition of 5% alumina particles was found to strengthen polyester composites as indicated by a morphological change from the unreinforced composites. However, the presence of 10% alumina particles promoted the formation of voids and agglomeration in the SEM images.

Wu and Hao (2019) observed the reinforcement of polylactic acid (PLA)/sisal fibers (SF) composites by incorporating a commercial grade epoxy-functionalized oligomer Joncryl ADR[®]-4368 (ADR) and poly (butylene-adipate-terephthalate) (PBAT) resin. SEM images revealed that part of the polymer matrix concentrated on the sisal fiber surface and welded to the PLA matrix to

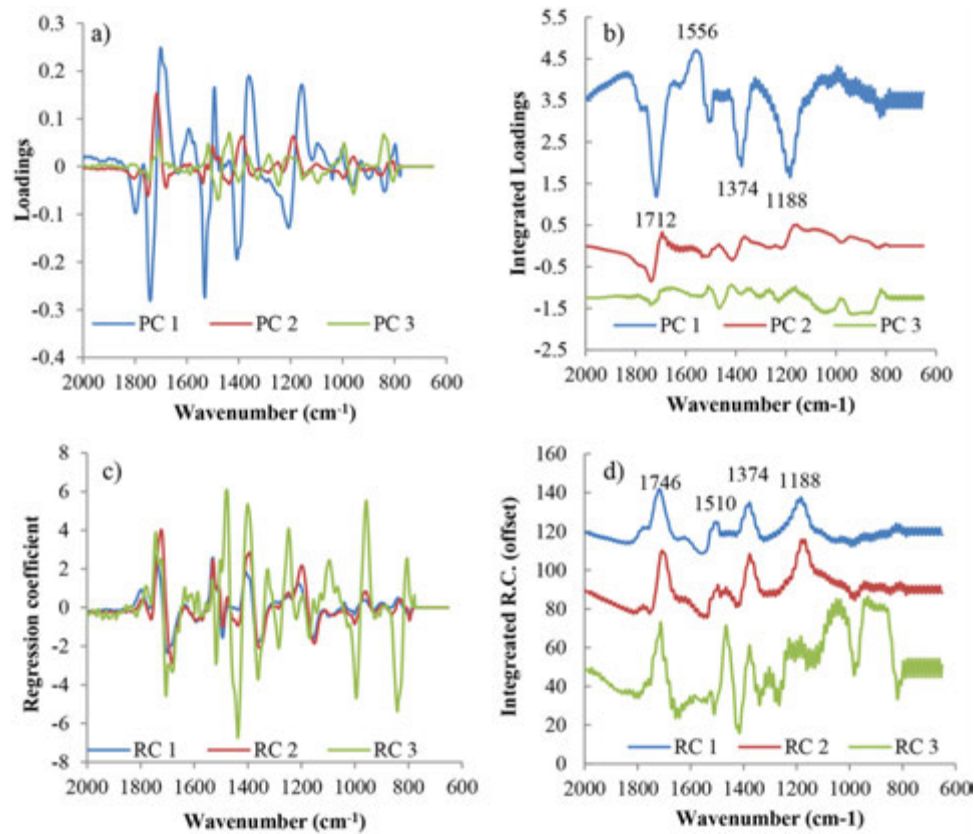


Fig. 2 Results of PCR analysis of IR spectra collected from calibration set samples after thermal exposure. (a) First three principal components loadings (b) First three integrated loadings. (c) First three regression coefficients. (d) First three integrated regression coefficients. Adapted from Toivola, R., Afkhami, F., Baker, S., McClure, J., Flinn, B.D., 2018. Detection of incipient thermal damage in carbon fiber-bismaleimide composites using hand-held FTIR. *Polymer Testing* 69, 490–498.

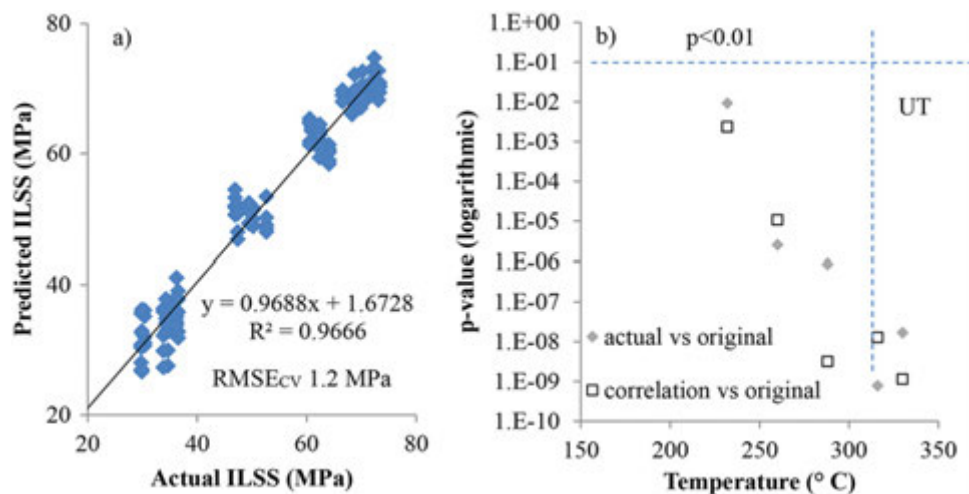


Fig. 3 (a) Correlation between PCR calibration model ILSS predictions and actual ILSS. (b) Student's *t*-test *p*-value for ILSS compared to original ILSS value. Horizontal dashed line " $p < 0.01$ " indicates *p*-value threshold of 0.01; Vertical dashed line 'UT' indicates exposures that cause damage detected by ultrasonic scan. Adapted from Toivola, R., Afkhami, F., Baker, S., McClure, J., Flinn, B.D., 2018. Detection of incipient thermal damage in carbon fiber-bismaleimide composites using hand-held FTIR. *Polymer Testing* 69, 490–498.

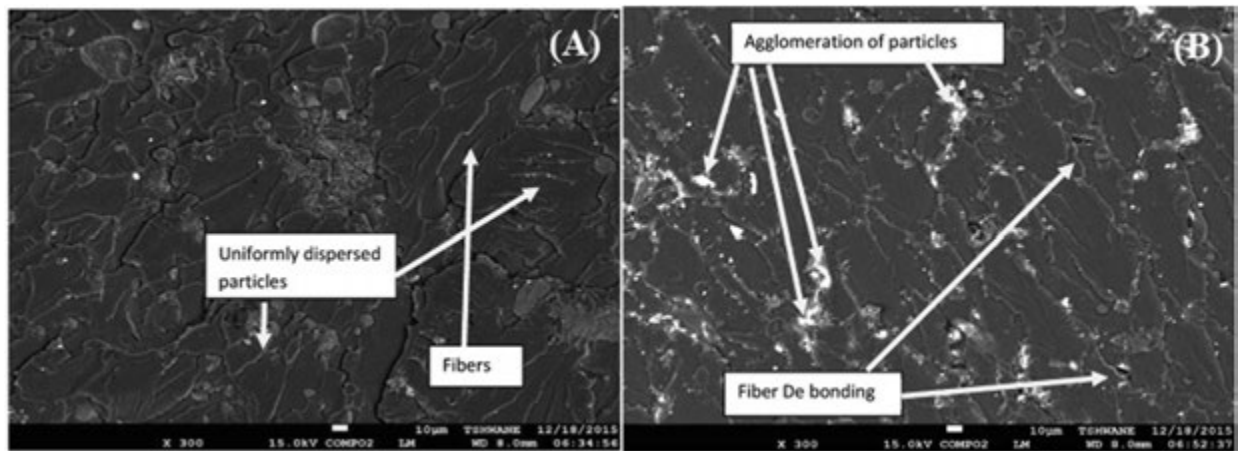


Fig. 4 Fracture surface of (a) treated and (b) untreated PKSF/PCP reinforced epoxy composites. Adapted from Oladele, I.O., Ibrahim, I.O., Adediran, A.A., *et al.*, 2020. Modified palm kernel shell fiber/particulate cassava peel hybrid reinforced epoxy composites. Results in Materials 5, 100053.

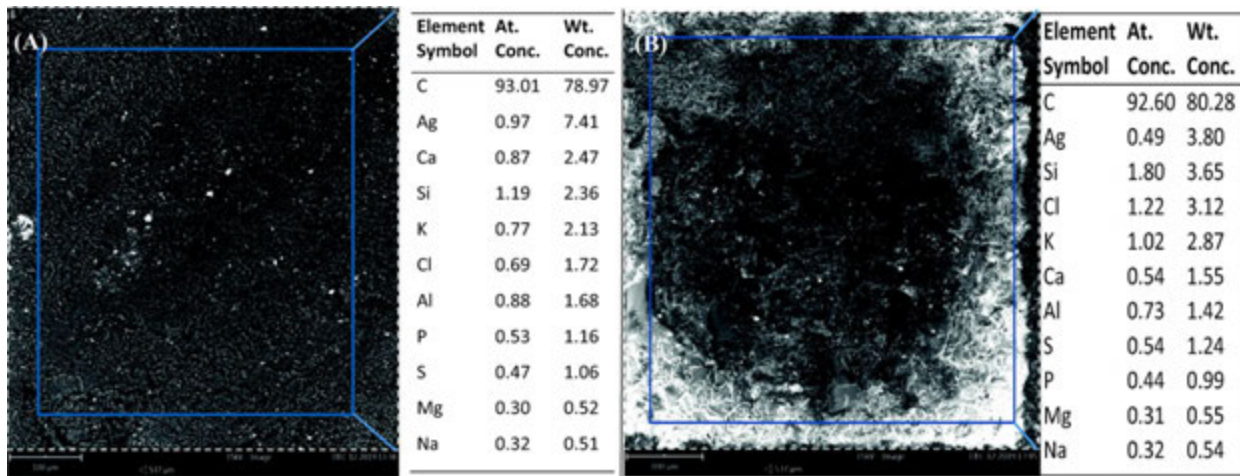


Fig. 5 SEM-EDX results of (a) charcoal reinforced and (b) unreinforced polyester matrix composites. Adapted from Akaluzia, R.O., Edoziuno, F.O., Adediran, A.A., *et al.*, 2021. Evaluation of the effect of reinforcement particle sizes on the impact and hardness properties of hardwood charcoal particulate-polyester resin composites. Materials Today: Proceedings 38, 570–577. Available at: <https://doi.org/10.1016/j.matpr.2020.02.980>.

form a self-welded fiber structure in PLA/PBAT/SF/ADR composites. Many broken fibers in the tensile fracture as shown in the SEM images suggested that ADR improves the interfacial interaction between fibers and polymer matrix, as well as between PLA and PBAT. Likewise, Oladele *et al.* (2020) observed a smoother surface for treated palm kernel shell fiber (PKSF) and particulate cassava peel (PCP) hybrid reinforced epoxy composites than the untreated one (Fig. 4). SEM micrograph of the untreated composites showed more particles at the fractured surface, indicating weak interfacial reaction and bonding between the untreated fiber and the epoxy matrix.

Energy dispersive X-ray spectroscopy (EDX), a rapid and non-invasive technique, has been used to complement SEM analysis through elemental characterization of composites chemical compositions. X ray emission from elements are dispersed based on the emission energies into separate channels that are expressed as peaks in a EDX spectrum. The number of peaks appeared for an individual element relies on the complexity of the electronic structure. Usually, heavier elements with more electron shells produce more emission peaks and complicated spectra. Therefore, EDX can be used for both qualitative and quantitative analyses. Moreover, EDX can provide a mapping of the spatial distribution of certain elements on a SEM micrograph. However, the penetration of X ray beam into the sample may excite the areas below the surface that are not shown in the SEM image. This may produce misleading results of EDX analysis.

Apart from a rough surface and an homogenous dispersion of reinforced particles observed in SEM micrographs, EDX characterization was employed by Akaluzia *et al.* (2021) to show an increase in the contents of calcium, silicon, potassium and aluminum in the polyester matrix reinforced by hardwood charcoal particles (Fig. 5).

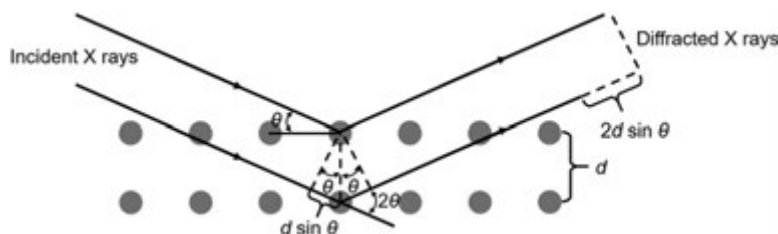


Fig. 6 Bragg's law and diffraction.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) analysis gains attention in the characterization of PMC to reveal the information of crystallinity and structural conformation of materials. XRD works based on the principle of elastic collisions between the incoming X ray beam and a particle that cause scattering of the reflected beam in all directions. The scattering pattern appears as peaks due to the constructive interference of the reflected beam along certain angles. This simple scattering can be explained by Bragg's law as shown in Fig. 6 (Bragg, 1913) and expressed by the following equation:

$$n\lambda = 2d\sin\theta$$

where n is any integer, λ is wavelength, d is the vector representing the displacement between reflection sites and θ is the angle between the reflected wave and the plane formed by the material's surface. XRD is an accurate and non-destructive analysis that requires only minimal amounts of sample and sample preparation (Schnablegger and Singh, 2011).

X-ray structural investigations can be performed at different approaches depending on the diffraction angles. The typical XRD or wide angle X-ray scattering (WAXS) has a shorter distance between the sample and detector, allowing diffraction measurements at a larger angle. While small angle X-ray scattering (SAXS) allows the detection of scattered X rays at a low angle which is beneficial for sample with large structural units (structure features with large repeat distances).

XRD analysis can be used to detect the presence of materials through identification of the fingerprints of the spectrum. Latief *et al.* (2019) confirmed the addition of alumina particles to the polyester matrix via the strong alumina peaks present in the XRD diffractograms. XRD data was used by Mahendran *et al.* (2016) to confirm the incorporation of graphene oxide sheets in the poly(vinyl alcohol (PVA)/poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS)/GO composites.

In addition, XRD analysis has been used to determine the crystallinity of composites because the degree of crystallinity can affect the mechanical properties of composites. Spahr and Schultz (1990) determine the degree of crystallinity in the poly(aryl-ether-ether-ketone) matrix-carbon fiber composites using WAXS. Volkova and Kalistratova (2015) examined the loss of crystallinity of polytetrafluoroethylene (PTFE) composites with carbon fiber, bronze and molybdenum disulfide at a temperature more than 555K. This is indicated in the disappearance of peaks in the XRD diffraction spectrum. Apart from observing the degree of crystallinity, Caban and Nitkiewicz (2007) revealed the polymorphic behavior of polypropylene in the glass fiber-polypropylene composites using both SAXS and XRD analyses. XRD spectrum revealed the polymorphous α types (monoclinic) or β (hexagonal) of polypropylene and polypropylene smectic phase (amorphous) in the composites. Also, glass fibers was seen to reduce the crystallinity degree of the polymeric matrix. In another study, Chethan *et al.* (2018) reported the changing of α to β phase of polyvinylidene fluoride (PVDF) matrix in the XRD diffractograms when nickel coated multi-walled carbon nanotubes (Ni-MWNT) and graphitized carbon nanofibers (GCNF) were added as nanofillers. This result supported the findings of IR spectroscopic and thermal analysis.

Thermal Analysis

Differential scanning calorimetry (DSC) is a common thermal analysis to investigate the thermal behavior of a sample. The basic principle of DSC works by measuring the temperature difference between a sample and a reference during heating, cooling or holding isothermally. By applying a heat signal to a sample, the response is measured as energy changes of thermal events such as melting, crystallization, glass transition and degradation over a temperature range or time period. Similar to FTIR analysis, thermal characterization using DSC requires minimal or no sample preparation and quick measurement can be done easily with a small quantity of sample. However, this technique is a destructive analysis.

In general, there are two types of DSC instruments: power compensation and heat flux. Power compensation DSC has two separate furnaces for the sample and reference with a temperature sensor placed in a bridge circuit. The temperature difference between these two furnaces is maintained at zero or near-zero through an electrical supply to the sample furnace at a different power. On the other hand, heat flux DSC has both sample and reference pans placed symmetrically within a furnace with a thermocouple in close contact with each pan. This design has a similar heat flow from the furnace to the sample and reference. This type of DSC is more commonly found.

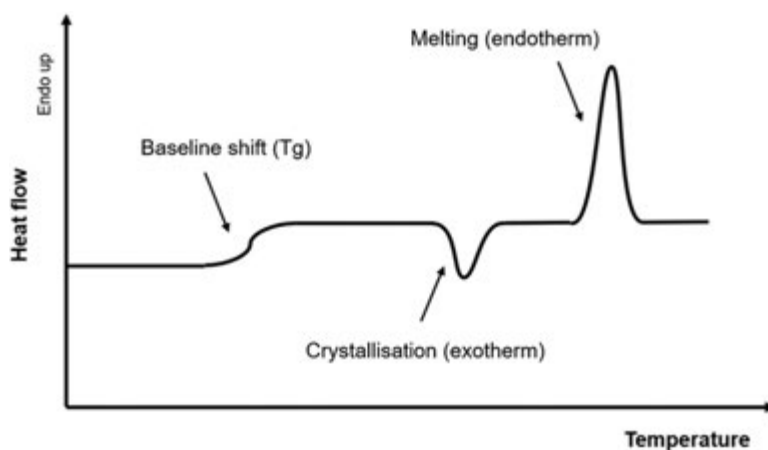


Fig. 7 DSC thermograms of semi-crystalline polymers.

The heat flow (dQ/dt) from each pan is represented by the equation below.

$$\frac{dQ}{dt} = \frac{\Delta T}{R}$$

where Q is the heat, t is the time, ΔT is the temperature difference between the furnace and the pan and R is the thermal resistance of the heat path between the furnace and the pan.

The heat flow signal is determined by the heat capacity (C_p) involved during heating. Heat capacity is the energy required to raise the temperature of the sample by one degree in temperature. The equation for the DSC signal may be expressed by

$$\frac{dQ}{dt} = C_p \frac{dT}{dt}$$

Therefore, heat flow into the sample (endotherms) or out of the sample (exotherms) as a function of temperature or time is presented in DSC thermograms in the unit of mW. Thermal transitions are shown usually as peaks (e.g., melting) or steps in the baseline (e.g., glass transition). The data shown in DSC thermograms have the direction of heat flow with either endotherms or exotherms up.

Fig. 7 shows a typical DSC thermogram of thermoplastic semi-crystalline polymers such as polyvinyl chloride, polypropylene and PEEK commonly used in PMC. On heating, temperature increases at a constant rate. The crystalline structure breaks down when melting occurs and a change in its heat capacity is observed. This causes the formation of a large melting endotherm. In a semi-crystalline polymer, there is a portion of the polymer available in the amorphous form. This gives rise to glass transition (T_g) which does not involve a latent heat. The T_g is a baseline shift transition where the polymer chains become plastic or rubbery. An exotherm above the T_g may occur indicating the crystallization, especially when crystallization does not happen in its maximum capacity during cooling.

The addition of Ni-MWNT and GCNF as nanofillers in PVDF matrices increases both melting point (heating scan) and crystallization rate (cooling scan) of the polymer (Chethan *et al.*, 2018). This suggested a higher thermal stability of the composites.

Apart from its frequent use in determining melting and glass transition temperatures, DSC can be used to deduce the crystallinity behavior and the interaction of the components in the PMC which are closely related to the mechanical properties of PMC. The crystallinity of epoxy composites was found reduced when curaura fibers are added into the matrix (Barcelos *et al.*, 2016). The decreased crystallinity was observed in the reduction of melting endotherm of epoxy at 138°C, indicating the transformation of crystalline epoxy matrix into amorphous state due to the presence of curaura fibers.

Rubab *et al.* (2014) studied the curing behavior of epoxy-titania composite using DSC analysis. A complete crosslinking of epoxide groups with the amine monomers during curing process was indicated by a shift of glass transition from below zero to above 40°C. This also showed that the movement of polymer chains are restricted at the T_g temperature below 0°C.

DSC analysis may be accompanied by thermogravimetric analysis (TGA). TGA measures the weight change of a sample as a function of time or temperature. This analytical method is invasive but straightforward which is usually used to determine thermal and oxidative stability of a PMC. The weight changes are presented in the percentage of weight loss in typical TGA curve and first derivative trace or DTG can provide a better visualization of the data.

TGA allows empirical differentiation of the thermal load in thermal degradation of PMC, especially with an intermediate thermal damage or a rapid heat-up when thermal equilibrium is not reached within the matrix (Eibl, 2017). The same study also employed chemometric analysis to estimate residual strength and to predict duration and temperature of a thermal pre-load using TGA but less accurate prediction than IR spectroscopy. In addition, TGA showed the stability of PVA/PAMPS/GO composites up to 170°C and identified three major mass losses that accounted for the materials present in the composites (Mahendran *et al.*, 2016).

Mechanical and Physicochemical Properties of PMC by Types

Polypropylene (PP) Based Composites

PP based PMC have good mechanical properties, moderate dimensional stability, high temperature of thermal deformation and flame resistance. Furthermore, PP based PMC can be recycled. The recovered PP shows a higher density, a lower porosity and a high water absorption property with a high dimensional stability in comparisons to the composites and native PP (Shubhra *et al.*, 2011). Haydar and Beg (2014) has developed a coir-fiber-reinforced PP based unidirectional composites using compression molding method. The PMC has shown better mechanical properties in terms of tensile strength, tensile modulus and impact strength of the unidirectional composites, especially with a higher fiber loading until the optimum loading, thereafter the mechanical properties reduced with higher fiber loading. The optimum loading reported is 30 wt% coir. The coir-fiber reinforced PP based PMC was treated with tetramethoxy orthosilicate to improve the adherence of matrices and reinforced fiber (Haydar and Beg, 2014).

Polyethylene (PE) Based Composites

The incorporation of maize fibers into PE based composite such as HDPE can improve the thermal and mechanical properties of PMC by decreasing the thermal diffusivity and thermal conductivity (Trigui *et al.*, 2013). HDPE incorporated with hybridized kenaf and pineapple leaf fibers (PALF) have also been reported to provide a higher tensile strength and Young's modulus compared to HDPE with kenaf leaf fibers alone. This is due to a higher cellulose content of the hybridized fibers even though kenaf fibers was reported to improve impact and water absorption properties of the PMC. By hybridization of both fibers, the PMC can enjoy the combination improvement in mechanical and water absorption property (Aji *et al.*, 2012). Another study by Chollakup *et al.* (2011) revealed that longer PALF showed a higher tensile strength of the HDPE based PMC than shorter PALF due to an increased interfacial bonding and a more homogenous dispersion of long PALF. Bagasse fibers have also been used as reinforced fibers in both low density polyethylene (LDPE) and HDPE based PMC. When the bagasse fiber amount exceeds 50% in LDPE and HDPE, a reduction in mechanical and physical properties of the PMC was observed (Youssef *et al.*, 2009).

Polystyrene (PS) Based Composites

Sugar palm fibers have been used as reinforced fibers in PS based composites. Sapuan and Bachtiar (2012) has compared the impact of incorporation of five different weight percentages (10–50 wt%) of sugar palm fiber into PS using melt mixer and hot press. The results showed that higher sugar palm fiber contents resulted in higher tensile strength and Young's modulus of the high impact PS.

Polyvinyl Chloride (PVC) Based Composites

PVC is a common and high demand material in construction sector due to its compatibility with most natural fibers, low cost, high durability, chemical and flame resistance. Coconut fiber reinforced PVC/acrylonitrile styrene acrylate blends have been developed and the composite showed a higher impact strength and thermal properties with increasing of fiber content (Jiang and Kamdem, 2004).

Polyesters Based Composites

Polyester/natural fiber (banana/sisal) reinforced with hybrid pineapple leaf fiber and glass fiber were developed and compared. The two samples were evaluated for a constant total fiber loading 0.40 V_f by verifying the ratio of reinforced fiber. It was reported that the chemical treatment of the reinforced fiber showed a reduction in composite thermal contact resistance. (Idicula *et al.*, 2006). Sisal-jute-glass reinforced polyester composites have been developed. The study showed improvement in mechanical properties such as tensile strength, flexural strength, and impact strength. The result suggested that Sisal-jute-glass reinforced polyester composites can be used as alternate material to replace pure glass (Ramesh *et al.*, 2013).

A biodegradable aliphatic polyester reinforced with bagasses treated with 1%–5% sodium hydroxide and 1% acetic acid solution have been developed and characterized. The PMC showed improved flexural, impact and water absorption properties when the reinforced fibers were used in the range of 0%–20% v/v. The PMC serves as an alternative to replace the original polyester fiber (Cao *et al.*, 2006).

Epoxy Based Composites

Epoxy is a common polymer used in lamination, adhesives, coatings, and advanced composite surfaces due to the excellent mechanical and chemical properties, corrosion resistance, good thermal and dimensional stability (Ren *et al.*, 2008). Hybridization of epoxy composite with oil palm empty fruit branch (EFB)/jute fibers demonstrated better mechanical and flexural strengths than the untreated composites (Jawaid *et al.*, 2011a,b). The use of natural fibers such as EFB/jute fibers into reinforced

composites also reduces the environmental waste. The tensile properties of these hybrid composites showed increase in jute fiber content imparted higher strength than the oil palm–epoxy composites.

Conclusion

The blending of different polymer matrices with a variation of reinforcing fibers have brought tremendous significant improvements in the mechanical and physicochemical properties of PMC. Improvement in the properties is due to the reinforcement contributed by the reinforced fiber content. This overview has provided an insight on the general mechanical and physicochemical properties of PMC by giving examples of various types of PMC. Improvement of the mechanical properties such as strength, stiffness and impact strength has produced newer materials for the advancement in industry. The polymer matrix composites have several advantages, such as low cost, low density and lesser abrasiveness. More research is required to explore the scope and limitations of these materials.

References

- Agrebi, F., Ghorbel, N., Bresson, S., Abbas, O., Kallel, A., 2019. Study of nanocomposites based on cellulose nanoparticles and natural rubber latex by ATR/FTIR spectroscopy: The impact of reinforcement. *Polymer Composites* 40 (5), 2076–2087.
- Aji, I.S., Zainudin, E.S., Abdan, K., Sapuan, S.M., Khairul, M.D., 2012. Mechanical properties and water absorption behavior of hybridized kenaf/pineapple leaf fibre-reinforced high-density polyethylene composite. *Journal of Composite Materials* 47 (8), 979–990.
- Akaluzia, R.O., Edoziuno, F.O., Adediran, A.A., *et al.*, 2021. Evaluation of the effect of reinforcement particle sizes on the impact and hardness properties of hardwood charcoal particulate-polyester resin composites. *Materials Today: Proceedings* 38, 570–577. <https://doi.org/10.1016/j.matpr.2020.02.980>.
- Barcelos, M.A., Ribeiro, C.G.D., Ferreira, J., *et al.*, 2016. Characterization of thermal behavior of epoxy composites reinforced with curaua fibers by differential scanning calorimetry. In: Ikhamyies, S.J., Li, B., Carpenter, J.S., *et al.* (Eds.), *Characterization of Minerals, Metals, and Materials*. Cham: Springer International Publishing, pp. 403–407.
- Bragg, W.L., 1913. The diffraction of short electromagnetic waves by a crystal. *Proceedings of the Cambridge Philosophical Society* 17, 43–57.
- Caban, R., Nitkiewicz, Z., 2007. Investigations of the structure of composites of PP/GF by means of X-ray methods. *Journal of Achievements in Materials And Manufacturing Engineering* 23 (1), 55–58.
- Cao, Y., Shibata, S., Fukumoto, I., 2006. Mechanical properties of biodegradable composites reinforced with bagasse fibre before and after alkali treatments. *Composite Part A: Applied Science and Manufacturing* 37 (3), 423–429. <https://doi.org/10.1016/j.compositesa.2005.05.045>.
- Cao, Y., Wu, Y., Cent, J., 2008. Evaluation of statistical strength of bamboo fiber and mechanical properties of fiber reinforced green composites. *Journal of Central South University of Technology* 15, 5647.
- Cecen, V., Seki, Y., Sarikanat, M., Tavman, I., 2008. FTIR and SEM analysis of polyester- and epoxy-based composites manufactured by VARTM process. *Journal of Applied Polymer Science* 108, 2163–2170.
- Chethan, P.B., Renukappa, N.M., Sanjeev, G., 2018. Preparation and crystalline studies of PVDF hybrid composites. *AIP Conference Proceedings* 1942, 050066.
- Chollakup, R., Tantatherdam, R., Ujjin, S., Sriroth, K., 2011. Pineapple leaf fiber reinforced thermoplastic composites: Effects of fiber length and fiber content on their characteristics. *Journal of Applied Polymer Science* 119, 1952–1960. <https://doi.org/10.1002/app.32910>.
- Chua, M., Chu, C.K., Teo, C., Lau, D., 2015. Patient-specific carbon nanocomposite tracheal prosthesis. *International Journal of Artificial Organs* 38 (1), 31–38. <https://doi.org/10.5301/ijao.5000374>.
- Dang, Z.M., Zhang, B., Li, J.G., Zha, J.W., Hu, G.H., 2012. Copper particles/epoxy resin thermosetting conductive adhesive using polyamide resin as curing agent. *Journal of Applied Polymer Science* 126 (3), 815–821.
- Eibl, S., 2017. Comparison of surface and bulk analytical techniques for the distinct quantification of a moderate thermal pre-load on a carbon fibre reinforced plastic material. *Polymer Degradation and Stability* 135, 31–42.
- Eibl, S., Wolfrum, J., 2012. Prospects to separately estimate temperature and duration of a thermal pre-load on a polymer matrix composite. *Journal of Composite Materials* 47, 3011–3025.
- Geng, D.B., Zeng, L.M., Li, Y., Fu, Q.Z., Hu, B., 2007. Effect of nano-SiO₂ on Bismaleimide composite. In: *Proceedings of the International Conference on Smart Materials and Nanotechnology in Engineering*, 64234Z. <https://doi.org/10.1117/12.780097>.
- Giorgini, L., Benelli, T., Mazzocchi, L., *et al.*, 2015. Recovery of carbon fibers from cured and uncured carbon fiber reinforced composites wastes and their use as feedstock for a new composite production. *Polymer Composites* 36 (6), 1084–1095.
- Gojny, F.H., Wichmann, M.H.G., Köpke, U., Fiedler, B., Schulte K., 2004. Carbon nanotube-reinforced epoxy-composites: Enhanced stiffness and fracture toughness at low nanotube content. *Composites Science and Technology* 64 (15), 2363–2371.
- Haydar, U.Z., Beg, M.D.H., 2014. Preparation, structure, and properties of the coir fiber/polypropylene composites. *Journal of Composite Materials* 48, 3293–3301.
- He, H.W., Gao, F., 2015. Effect of fiber volume fraction on the flexural properties of unidirectional carbon fiber/epoxy composites. *International Journal of Polymer Analysis and Characterization* 20 (2), 180–189. <https://doi.org/10.1080/1023666X.2015.989076>.
- Idicula, M., Boudenne, A., Umadevi, L., *et al.*, 2006. Thermophysical properties of natural fiber reinforced polyester composites. *Composites Science and Technology* 66 (15), 2719–2725. <https://doi.org/10.1016/j.compscitech.2006.03.007>.
- Jawaid, M., Khalil, H.P.S.A., Abu Bakar, A., 2011a. Hybrid composites of oil palm empty fruit bunches/woven jute fiber: Chemical resistance, physical, and impact properties. *Journal of Composite Materials* 45, 2515–2522. <https://doi.org/10.1177/0021998311401102>.
- Jawaid, M., Khalil, H.P.S.A., Abu Bakar, A., 2011b. Woven hybrid composites: Tensile and flexural properties of oil palm-woven jute fibres based epoxy composites. *Materials Science and Engineering A* 528 (15), 5190–5195. <https://doi.org/10.1016/j.msea.2011.03.047>.
- Jiang, H., Kamdem, D.P., 2004. Development of poly(vinyl chloride)/wood composites. A literature review. *Journal of Vinyl and Additive Technology* 10, 59–69. [https://doi.org/10.1002/\(ISSN\)1548-0585](https://doi.org/10.1002/(ISSN)1548-0585).
- Keith, J.M., King, J.A., Lenhart, K.M., Zimny, B., 2007. Thermal conductivity models for carbon/liquid crystal polymer composites. *Journal of Applied Polymer Science* 105 (6), 3309–3316.
- Larbi, S., Bensaada, R., Bilek, A., Djebali, S., 2015. Hygrothermal ageing effect on mechanical properties of FRP laminates. *AIP Conference Proceedings* 1653, 020066-1–020066-7. <https://doi.org/10.1063/1.4914257>.
- Latief, F.H., Chafidz, A., Junaedi, H., Alfazan, A., Khan, R., 2019. Effect of alumina contents on the physicomechanical properties of alumina (Al₂O₃) reinforced polyester composites. *Advances in Polymer Technology* 2019. <https://doi.org/10.1155/2019/5173537>.

- Mahendran, R., Sridharan, D., Santhakumar, K., Gnanasekaran, G., 2016. Green route fabrication of graphene oxide reinforced polymer composites with enhanced mechanical properties. *Journal of Nanoscience* 2016. 6410295.
- Masek, A., Diakowska, K., Zaborski, M., 2016. Physico-mechanical and thermal properties of epoxidized natural rubber/poly(lactide) (ENR/PLA) composites reinforced with lignocellulose. *Journal of Thermal Analysis And Calorimetry* 125, 1467–1476.
- Mazur, R.L., Oliveira, P.C., Rezende, M.C., Botelho, E.C., 2014. Environmental effects on viscoelastic behavior of carbon fiber/PEKK thermoplastic composites. *Journal of Reinforced Plastics and Composites* 33 (8), 749–757.
- Mohanty, A., Srivastava, V.K., 2015. Effect of alumina nanoparticles on the enhancement of impact and flexural properties of the short glass/carbon fiber reinforced epoxy based composites. *Fibers and Polymers* 16, 188–195.
- Oladele, I.O., Ibrahim, I.O., Adediran, A.A., *et al.*, 2020. Modified palm kernel shell fiber/particulate cassava peel hybrid reinforced epoxy composites. *Results in Materials* 5. 100053.
- Ram, R., Rahaman, M., Khastgir, D., 2014. Mechanical, electrical, and dielectric properties of polyvinylidene fluoride/short carbon fiber composites with low-electrical percolation threshold. *Journal of Applied Polymer Science* 131 (3), <https://doi.org/10.1002/app.39866>.
- Ramesh, M., Palanikumar, K., Hemachandra Reddy, K., 2013. Mechanical property evaluation of sisal-jute-glass fiber reinforced polyester composites. *Composites Part B: Engineering* 48, 1–9. <https://doi.org/10.1016/j.compositesb.2012.12.004>.
- Ren, H., Sun, J.Z., Zhao, Q., Zhou, Q.Y., 2008. Synthesis and characterization of a novel heat resistant epoxy resin based on N, N0-bis(5-hydroxy-1-naphthyl) pyromellitic diimide. *Polymer* 49, 5249–5253. <https://doi.org/10.1016/j.polymer.2008.09.047>.
- Rubab, Z., Afzal, A., Siddiqi, H.M., Saeed, S., 2014. Preparation, characterization, and enhanced thermal and mechanical properties of epoxy-titania composites. *The Scientific World Journal* 2014.515739. <https://doi.org/10.1155/2014/515739>.
- Sapuan, S.M., Bachtiar, D., 2012. Mechanical properties of sugar palm fibre reinforced high impact polystyrene. *Composites Procedia Chemistry* 4, 101–106. <https://doi.org/10.1016/j.proche.2012.06.015>.
- Schnablegger, H., Singh, Y., 2011. *The SAXS Guide*, second ed. Austria: Anton Paar GmbH.
- Semoto, T., Tsuji, Y., Tanaka, H., Yoshizawa, K., 2013. Role of edge oxygen atoms on the adhesive interaction between carbon fiber and epoxy resin. *Journal of Physical Chemistry* 117 (47), 24830–24835.
- Shubhra, Q.T.H., Alam, A.K.M.M., Quaiyyum, M.A., 2011. Mechanical properties of polypropylene composites: A review. *Journal of Thermoplastic Composite Materials* 26 (3), 362–391.
- Song, J.B., Liu, X.S., Zhang, Y.H., Huang, B., Yang, W.B., 2016. Carbon-fiber-reinforced acrylonitrile–styrene–acrylate composites: Mechanical and rheological properties and electrical resistivity. *Journal of Applied Polymer Science* 133 (13), <https://doi.org/10.1002/app.43252>.
- Spahr, D.E., Schultz, J.M., 1990. Determination of matrix crystallinity of composites by X-ray diffraction. *Polymer Composites* 11, 201–210.
- Subramaniam, A.S., Tey, J.N., Zhang, L., *et al.*, 2016. Synergistic bond strengthening in epoxy adhesives using polydopamine/MWCNT hybrids. *Polymer* 82 (1), 285–294.
- Tabačiarová, J., Krajčí, J., Pionteck, J., *et al.*, 2016. Styrene butadiene rubber/carbon filler-based vapor sensors. *Macromolecular Chemistry and Physics* 217 (10), 1149–1160.
- Toivola, R., Afkhami, F., Baker, S., McClure, J., Flinn, B.D., 2018. Detection of incipient thermal damage in carbon fiber-bismaleimide composites using hand-held FTIR. *Polymer Testing* 69, 490–498.
- Tomioka, J.I., Kiguchi, K., Tamura, Y., Mitsuishi, H., 2011. Influence of temperature on the fatigue strength of compressed-hydrogen tanks for vehicles. *International Journal of Hydrogen Energy* 36 (3), 2513–2519.
- Tonetto, M.R., Pinto, S.C., Rastelli Ade, N., *et al.*, 2013. Degree of conversion of polymer-matrix composite assessed by FTIR analysis. *The Journal of Contemporary Dental Practice* 14, 76–79.
- Trigui, A., Karkri, M., Pena, L., *et al.*, 2013. Thermal and mechanical properties of maize fibers-high density polyethylene bio composites. *Journal of Composite Materials* 47, 1387–1397. <https://doi.org/10.1177/002198312447648>.
- Volkova, V.K., Kalistratova, L.F., 2015. X-ray diffraction analysis of structure of composite materials based on polytetrafluoroethylene during thermal exposure. *Inorganic Materials: Applied Research* 6, 411–413.
- Wang, C.J., Li, W., 2016. Preparation, characterization, and in vitro and vivo antitumor activity of oridonin-conjugated multiwalled carbon nanotubes functionalized with carboxylic group. *Journal of Nanomaterials* 2016, 1–7. <https://doi.org/10.1155/2016/3439419>.
- Wolfrum, J., Whitney, E., Eibl, S., 2016. Approaches to understand and predict the influence of rapid heat-up on degradation and strength of carbon fibre polymer matrix composites. *Journal of Composite Materials* 51, 2435–2447.
- Wu, H., Hao, M., 2019. Strengthening and toughening of polylactide/sisal fiber biocomposites via in-situ reaction with epoxy-functionalized oligomer and poly (butylene-adipate-terephthalate). *Polymers* 11, 1747.
- Yashas Gowda, T.G., Sanjay, M.R., Subrahmanya Bhat, K., *et al.*, 2018. Polymer matrix-natural fiber composites: An overview. *Cogent Engineering* 5 (1), 1446667. <https://doi.org/10.1080/23311916.2018.1446667>.
- Youssef, H.A., Ismail, M.R., Ali, M.A.M., Zahran, A.H., 2009. Studies on sugarcane bagasse fiber-thermoplastics composites. *Journal of Elastomers And Plastics* 41, 245–262. <https://doi.org/10.1177/0095244308095014>.
- Yunus, M., Alsoufi, M.S., 2018. Experimental investigations into the mechanical, tribological, and corrosion properties of hybrid polymer matrix composites comprising ceramic reinforcement for biomedical applications. *International Journal of Biomaterials* 2018.9283291. <https://doi.org/10.1155/2018/9283291>.

Further Reading

- Run, M., Hao, Y., He, Z., 2010. Studies on the isothermal crystallization kinetics and morphology of PTT/SGF composites. *Polymer Composites* 31 (6), 995–1002.

Processing of Polymers and Their Composites: A Review

Jaspreet Singh, Kulwinder Singh, and JS Saini, Thapar Institute of Engineering and Technology, Patiala, Punjab, India
Mohammed SJ Hashmi, Dublin City University, Dublin, Ireland

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Jaspreet Singh, Kulwinder Singh, Jaswinder S. Saini, Mohammed S.J. Hashmi, Processing of Polymers and Their Composites: A Review, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2018, doi:10.1016/B978-0-12-803581-8.11435-3.

Introduction

The word 'polymer' is the combination of two Greek words 'poly' and 'mers'. 'Poly' means many and 'mers' means parts. 'Mers' are the basic entity of polymer and when they link in the repetition they form a large molecule which is called polymer. Depending upon the types of 'mers' the polymer can be classified in many categories from the nature of polymer *i.e.*, natural or synthetic, thermoset or thermoplastic, polymer structure, its thermal behaviour, polymerization, and its preparative techniques [1].

The choice of individual polymer from the family of polymers for a particular application is difficult. Material properties, which are required, for particular application make it easy to choose a particular material. Moreover, the suitable processing technique for a particular application also help to choose a suitable polymeric material. The manufacturing technique to produce a part is chosen with respect to part design, low manufacturing cost and the type of the material to be used for that particular application from the family of polymeric materials. Number of processing techniques have been invented with their own advantages, disadvantages and applications [2].

Polymer materials and their composites have numerous applications due to their advantages over conventional materials [3,4]. Simple fabrication methods and low cost have made polymer matrix composites very popular. However, the use of polymers in comparison to polymer matrix composites as structural materials is very limited due to the difference of their mechanical properties. Composite materials have two phases, namely matrix and reinforcement. The different type of reinforcements are embedded into matrix in order to improve its properties with respect to its end use requirements. The applications of polymer matrix composites are mainly due to its high specific strength and specific modulus [5]. The applications of polymers matrix composites in the aerospace, marine and automotive industries are increasing day by day due to its properties such as low density, high specific strength, high specific stiffness, and high fracture resistance [6]. Whereas, the property of good corrosion resistance and chemically inertness not only make it suitable for marine boat bodies but also for chemical storage tanks, pipes as well as pressure vessels [7]. The applications of polymer matrix composites are attaining wide acceptance in the manufacturing of bridges due to lower weight, good fatigue impact and corrosion resistance of material [8]. Polymer matrix composite materials are the insulators and due to this property these are used in electrical appliances such as panels, housing and connectors [9]. All these properties also make it suitable for the biomedical applications [10].

Although there are number of parameters in polymer composite materials which influence their final properties but the change in material and the processing techniques are the most important ones. The processing techniques used to manufacture the polymer composites have many different variables which need to be controlled simultaneously to improve the performance of the material significantly. The optimization of different variables is crucial to enhance the properties of the composite in comparison to its parent materials [11]. Moreover, the part performance can be improved by the combination of two or more processing techniques together [12].

Besides shapes of the part, the choice of manufacturing processes depends upon type of material to be processed for a particular application. Polymers are broadly classified into two categories that is thermoplastic and thermosets. The processing techniques for both the materials are different and processing parameters are chosen and controlled accordingly. Table 1 shows the variability in different parameters for different types of materials.

Thermoplastic polymers have linear or branched chain molecules having strong intramolecular bonds but weak bonds between adjacent chains. They could be amorphous or semi crystalline in nature and can be processed by heating and pressing into desired shape. The advantage of these materials is that it can be easily reshaped under the effect of heat and pressure. On the other hand thermosetting polymers consists of cross-linked or three dimensional network structure with covalent bonds within all chains. Thermosets are formed by melting and then pouring into the mold to make a desired shape. Once they solidifies and they form 3-dimensional structure they cannot be reshaped. They decompose upon heating but do not soften [13]. The recycling property of thermoplastic materials has made it advantageous over the thermosetting materials [14]. However, as shown in Table 1, use temperature and solvent resistance of thermoset materials is more than that of thermoplastic materials. Since, the number of parameters need to be controlled while the manufacturing of composites with thermoset or thermoplastic matrix, fabrication of composites is a complex process.

Curing plays a very important role in the manufacturing of the component. Although curing of material depends upon many parameters, temperature and pressure for a particular time are the important parameters to be controlled for the transformation of resin (thermoset polymer) into final parts. Temperature initiates the chemical reaction and pressure force is used to flow the resin. The magnitude and duration of these process variables have a significant effect on the performance of the part to be produced for

Table 1 Comparison of characteristics of thermoplastic and thermoset polymers

Resin type	Process temperature	Process time	Use temperature	Solvent resistance	Toughness
Thermoset	Low	High	High	High	Low
Toughened thermoset	↑	↓	↑	↑	↓
Lightly crosslinked thermoplastic	High	Low	Low	Low	High
Thermoplastic					

SOURCE: Daniel R. Tenney, NASA Langley Research Center.

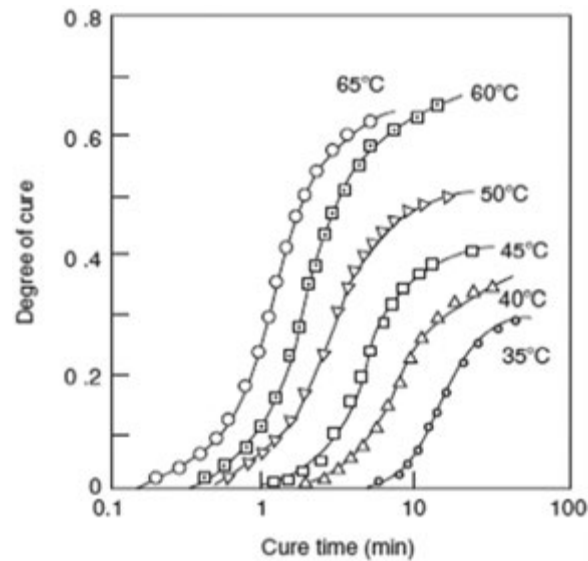


Fig. 1 Degree of cure variations with cure temperature and time for vinyl-ester. Reproduced from Han, C.D., Lem, K.W., 1984. Chemorheology of thermosetting resins. IV. The chemorheology and curing kinetics of vinyl ester resin. *Journal of Applied Polymer Science* 29 (5), 1879–1902. Reproduced from Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press.

structural applications. Since duration is the integral part of the cure cycle and it also defines the rate of production, the shortest cure cycle will increase production rate. In the processing of polymers and polymer matrix composites, resin is converted into matrix and cure cycle is associated with polymer or resin behaviour such as viscosity, resin flow, consolidation, degree of flow etc. Differential scanning calorimeter (DSC) experiments were performed to calculate the heat involved in curing process and to calculate degree of cure [15, 16]. Fig. 1 shows the degree of cure and cure time graph for vinyl-ester resin at different temperatures.

It is clear from figure that degree of cure is the function of both temperature and time, it increases as temperature or time of curing increases. However, the rate of cure decrease as the degree of cure reaches maximum value for a particular temperature. At low cure temperature, degree of cure is low in comparison to it at higher cure temperature. As cure temperature increases, the rate of cure also increases and leads to high degree of cure even at low time [17, 18].

Fig. 2 shows the viscosity variation of epoxy resin during isothermal curing. The initial viscosity of resin is very low. However, it is increased as the cycle time increases at a particular temperature, the time to increase the viscosity decreased as the cure temperature is increased [19, 20]. At early stage of curing the rate of increase of viscosity was low up to gel time, after gel time viscosity increased rapidly and resin was converted into matrix or solid mass.

In composite processing generally in liquid composite molding, proper flow of resin is required to produce void free parts. The viscosity of thermoset resins increases rapidly as curing reaction is initiated, and the simultaneous flow of resin with curing reaction may lead to voids and poor interlaminar adhesion. Permeability through fibre network is essential parameter which basically govern the resin flow through fibre network. Gebart [21] proposed permeability equations for unidirectional fibre network as following.

$$\text{In the fibre direction : } P_{11} = \frac{2d_f^2}{C_1} \frac{1 - V_f^3}{V_f^2} \quad (1)$$

$$\text{Normal to fibre direction : } P_{22} = C_2 \left(\sqrt{\frac{V_{fmax}}{V_f}} \right) \quad (2)$$

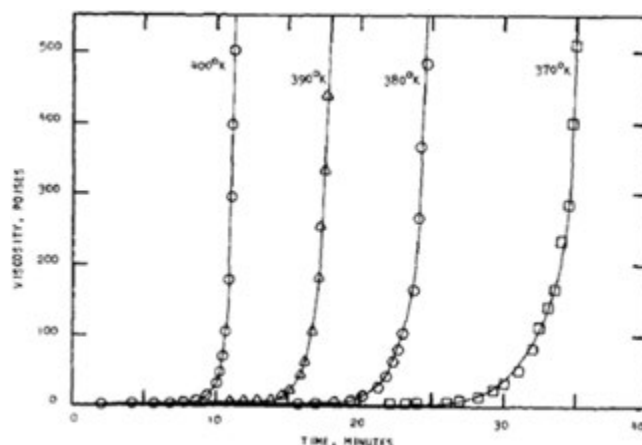


Fig. 2 Variation of viscosity during isothermal curing of epoxy. Reproduced from Kamal, M.R., 1974. Thermoset characterization for moldability analysis. *Polymer Engineering & Science* 14 (3), 231–239.

Where, d_f is the fibre diameter, V_f is the fibre volume fraction, C_1 is the hydraulic radius between the fibres and C_2 is a constant.

Hubert and Pourstrip [22] further investigated that good resin flow through fibre perform is not sufficient to produce consolidated part. Compaction pressure is also required to squeeze out air bubbles and to produce void-free parts.

Processing of Polymers and its Composites

There are numerous processing techniques which are available to manufacture the polymer and their composites. These techniques are developed in such a way that it would be able to produce part of different design parameters, different material properties as well as to minimize the defects while manufacturing. The use of fundamental science in the processing techniques have developed many new techniques as well as improved the existing techniques significantly [23]. Several researchers have worked on the use and optimization of the following processing techniques for different applications.

Injection Molding

Injection molding is a technique to transfer polymer materials into useful products of various shapes. It is a cost-effective method, and can produce complex shape parts not only with a high precision but also at a high production rate. Fig. 3 shows the schematic diagram of injection molding process which comprises a hydraulic unit, injection unit and clamping unit.

High production rate of injection molding process is closely associated with injection velocity. Yang and Gao [24] used an adaptive controller to control the injection velocity. The pole-placement technique was found to be suitable for different molding conditions. Shrinkage is the problem that is associated with injection molding process. If a hollow or a partially hollow part is to be produced by using injection molding technique then water assisted or gas assisted injection molding can overcome the problem of shrinkage. Although, process cycle for gas and water assisted injection molding is almost same, water assisted injection molding have several advantages over gas assisted injection molding. The cooling cycle of water assisted injection molding technique is less than gas assisted injection technology because of high thermal conductivity of water. Compaction of water is higher than that of gas because water is incompressible in nature. Water injection technology (WIT) can produce part with high internal surface than gas assisted injection molding. When the water is injected into the melt, its viscous front acts as a ram and this viscous front forces the molten material forward, and eventually helps to reduce defects in the final part [25].

Water assisted injection molding technology is of two types, partially filled (short-shot molding) and fully filled (full-shot molding) mold with polymer melt. After filling the polymer melt into the mold, water is injected into the core of polymer melt. The schematic diagram of water assisted injection molding is shown in Fig. 4.

Liu and Chen [26] used Taguchi method to optimize the process parameters of water assisted injection molding for thermoplastic composites. Optimization of parameters was done on the basis of length of water penetration into the core. In conventional injection molding process polymer melt starts to cool very rapidly as it enters the mold cavity and the molded part then undergoes a shrinkage. In water assisted injection molding water penetrates into the core of polymeric melt and pushes it against the mold wall which helps to minimize the shrinkage. Short-shot size were found to be significant parameter which affect the length of penetration. Liu and Chen [27] investigated the design of water injection pins. As the polymer melt is forced into the mold cavity, melt could stick to the small opening of water injection pins. Two type of rings were selected to study this behaviour. Result showed that ring type water pins have very less chance of sticking by polymer melt. However, due to limited volumetric flow rate the possibility of incomplete filling is severe. On the other hand the possibility of sticking of orifice type pins is very high. However, its larger hole diameter leads to complete filling of mold.

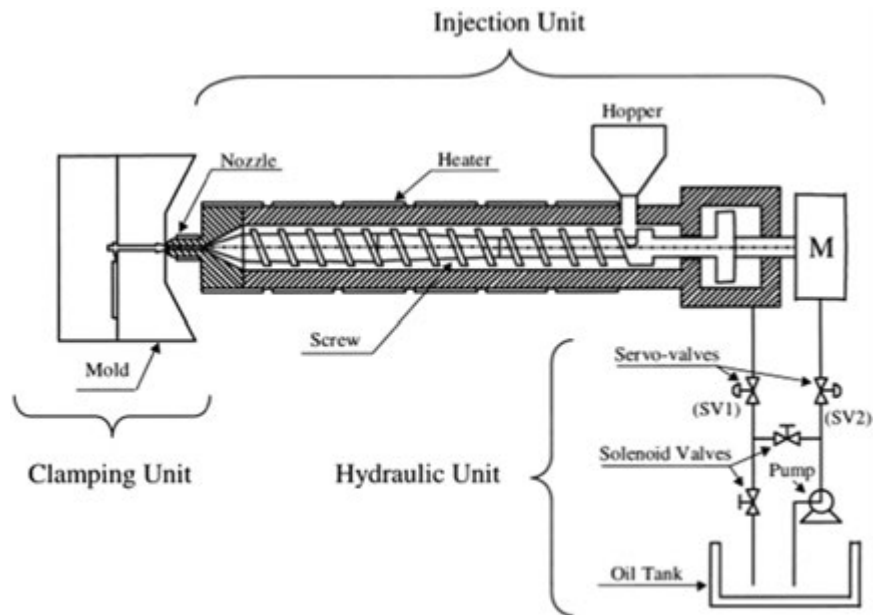


Fig. 3 Schematic diagram of injection molding machine. Reproduced from Yang, Y., Gao, F., 2000. Adaptive control of the filling velocity of thermoplastics injection molding. *Control Engineering Practice* 8 (11), 1285–1296.

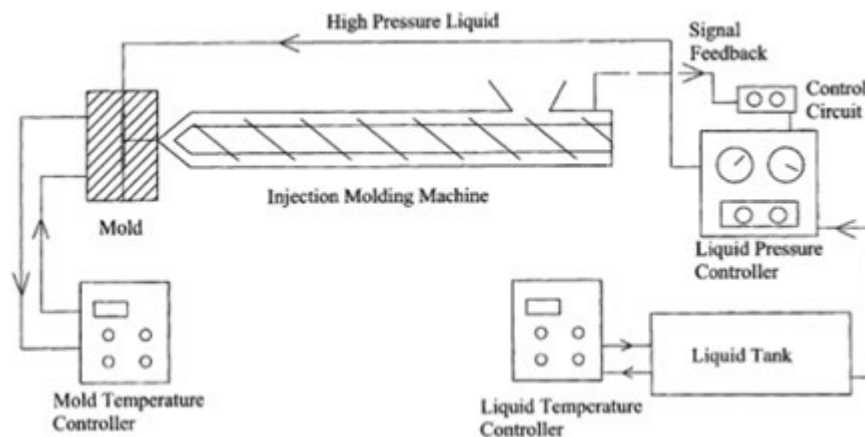


Fig. 4 The setup for water-assisted injection-molding. Reproduced from Liu, S.-J., Chen, Y.-S., 2004. The manufacturing of thermoplastic composite parts by water-assisted injection-molding technology. *Composites Part A: Applied Science and Manufacturing* 35 (2), 171–180.

Thin wall injection molding has many applications in electronic industry especially in micro-electro-mechanical systems. However, injection molding process for manufacturing parts with very low thickness is difficult and complicated. Song *et al.* [28] used Taguchi method to investigate the different process parameters as shown in Table 2. Table 3 shows the results of the filling area with respect to different parameters of injection molding process.

The result shows that by increasing injection rate the filling ratio increases. Higher melt temperature and injection pressure is also required in molding process to attain maximum filling of mold as shown in Figs. 5 and 6.

Filling volume was calculated by varying injection rate up to five values. The effect of melt temperature and injection pressure on filling volume was also investigated by varying melt temperature gradually from 190°C to 250°C and injection pressure from 50 MPa to 110 MPa as shown in Fig. 6. Ramakrishnan and Mao [29] studied the effect of injection molding process on the shrinkage of a polymer gear part. Taguchi orthogonal array design and ANOVA method was used to optimize the process parameters which were identified the most significant for volumetric shrinkage. Melt temperature was found to be most significant contributor for volumetric shrinkage followed by the pressure. Huang and Deng [30] investigated the effect of short-shot size, water pressure, melt temperature and water injection delay time on water penetration length. The orthogonal array of Taguchi method was used to find the optimal parameters resulting in maximum penetration length. Different levels of $L_9(3^4)$ orthogonal array were chosen as per Table 4.

Table 2 Levels table of factors

Factors	Levels		
	Level 1	Level 2	Level 3
A: Injection rate v (mm/s)	60	84	108
B: Injection pressure p (MPa)	85	95	105
C: Melt temperature θ ($^{\circ}\text{C}$)	220	230	240
D: Metering size h (mm)	7.0	7.5	8.0
E: Part thickness δ (mm)	0.2	0.1	–

Note: Song, M., *et al.*, 2007. Research on effects of injection process parameters on the molding process for ultra-thin wall plastic parts. *Journal of Materials Processing Technology* 187, 668–671.

Table 3 Project and results of experiment

No.	A: v (mm/s) 1	C: θ ($^{\circ}\text{C}$) 2	3	B: p (MPa) 4	D: h (mm) 5	6	7	E: δ (mm) 8	Results (area mm^2)
1	1 (60)	1 (220)		2 (95)	2 (7.5)			1 (0.2)	149.5
2	2 (84)	1		1 (85)	1 (7.0)			1	143.3
3	3 (108)	1		3 (105)	3 (8.0)			1	172.5
4	1	2 (230)		1	2			1	160.3
5	2	2		3	1			1	111.0
6	3	2		2	3			1	176.2
7	1	3 (240)		3	1			1	86.0
8	2	3		2	3			1	191.7
9	3	3		1	2			1	172.3
10	1	1		1	3			2 (0.1)	52.2
11	2	1		3	2			2	64.3
12	3	1		2	1			2	46.9
13	1	2		3	3			2	54.5
14	2	2		2	2			2	61.7
15	3	2		1	1			2	55.8
16	1	3		2	1			2	35.1
17	2	3		1	3			2	59.1
18	3	3		3	2			2	56.6
Sum of level 1	537.6	600.8		643	478.1			1362.8	
Sum of level 2	631.1	619.5		661.1	664.7			486.2	
Sum of level 3	680.3	628.7		544.9	706.2			–	
Dispersion R	142.7	27.9		116.2	228.1			876.6	

Note: Song, M., *et al.*, 2007. Research on effects of injection process parameters on the molding process for ultra-thin wall plastic parts. *Journal of Materials Processing Technology* 187, 668–671.

Short-shot size was found to be most significant parameter. However, short-shot size (68.5%), melt temperature of 220°C , water pressure of 9 MPa and water injection delay time of 5 s were the optimal parameters to maximize the water penetration length. The crystallinity of final product was also analysed by using differential scanning calorimetry (DSC) at the beginning and the end of the channel of curved pipe. Samples for DSC were taken from inner, middle and outer layer, maximum crystallinity was observed at the middle layer sample took from the beginning of curved pipe.

Pultrusion Process

The term pultrusion is the combination of two words “pull” and “extrusion”. It is the process in which fibres are pulled into resin and then allowed to pass through heated die. Pultrusion is a molding process for producing structural members of uniform cross-sectional area. Solid and hollow structures can be processed easily by the pultrusion process [31]. Advancement in manufacturing processes have made it compatible for the manufacturing of channels, beams, bars and many other profiles. Fig. 7 shows a schematic diagram of pultrusion line for producing polymer composites. Fibres from roving creels and mat creels are pulled into resin bath through a guide. After the impregnation of fibres into resin, the impregnated fibres are pulled into performer and then into a long die. Performer helps to squeeze out excess resin whereas curing and compaction is done in the die. At the end of the pultrusion line, pull blocks pull the cured parts from the die and it is cut from continues pultrusion line as per required length [32].

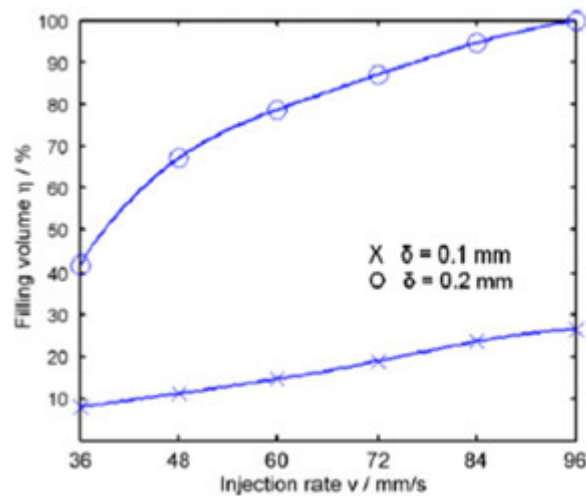


Fig. 5 Effects of part thickness to the molding. Reproduced from Song, M., *et al.*, 2007. Research on effects of injection process parameters on the molding process for ultra-thin wall plastic parts. *Journal of Materials Processing Technology* 187, 668–671.

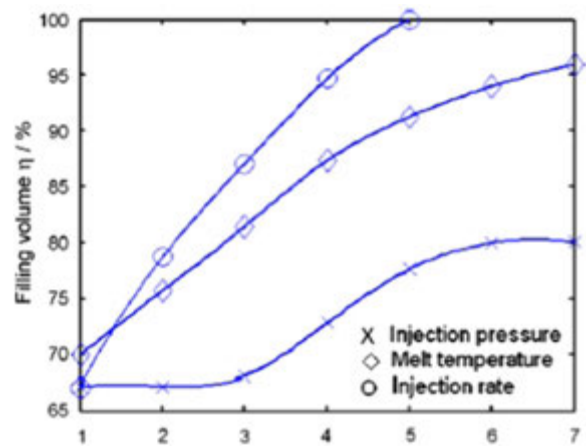


Fig. 6 Effects of process parameters to the molding. Reproduced from Song, M., *et al.*, 2007. Research on effects of injection process parameters on the molding process for ultra-thin wall plastic parts. *Journal of Materials Processing Technology* 187, 668–671.

Table 4 Factors and their levels in orthogonal experiment

Factors	Level		
	1	2	3
A: Short-shot size (%)	68.5	73.2	77.6
B: Melt temperature (°C)	210	220	230
C: Water pressure (MPa)	7	9	11
D: Water injection delay time (s)	1	3	5

Note: Huang, H.X., Deng, Z.W., 2008. Effects and optimization of processing parameters in water-assisted injection molding. *Journal of applied polymer science* 108 (1), 228–235.

Pultrusion have several advantages over other composite processing techniques as it could allow to produce any transportable length [33]. Moreover, the cost of product is very less in comparison to other processing techniques. Its cost is approximately 41% of the filament winding technique and 26% of the hand layup technique [34]. However, the part with non-uniform cross-section area and complex shapes cannot be produced by using the pultrusion technique. Moreover, poor dimensional accuracy and non-uniform curing problems are also associated with pultrusion technique [31].

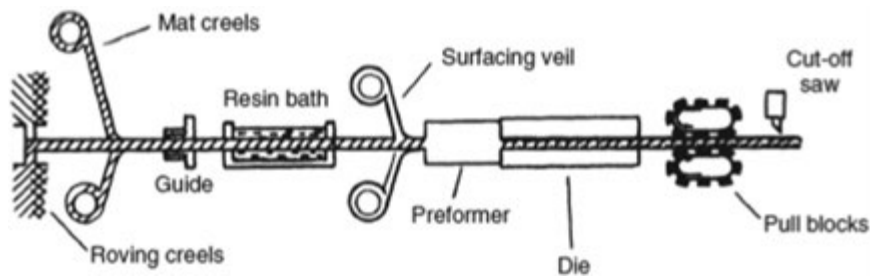


Fig. 7 Schematic of a pultrusion process. Reproduced from Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press.

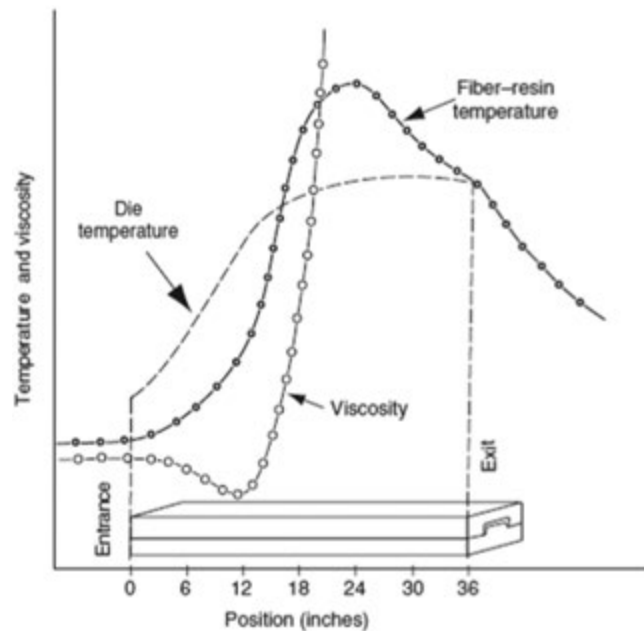


Fig. 8 Viscosity and temperature variations of a thermosetting resin in a pultrusion die. Reproduced from Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press.

In thermosetting pultrusion the mechanical properties of final product depends upon the degree of cure and its uniformity. Non-uniform curing of component during pultrusion leads to an inhomogeneous structure. There are number of parameters those effect the final properties of pultruded parts. Fibre wet-out, die temperature, die length, pulling speed and properties of fibre are the main process parameters required to control in order to produce final product with high quality. Fibre wet-out take place through capillary action and low resin viscosity as well as slow line speed increases the capillary action [35]. The die length, temperature and pulling speed are found to be responsible for the degree of cure of pultruded member, and are controlled to attain maximum degree of cure. Fig. 8 shows that resin viscosity decreased at the entrance of die and this aids to proper wet-out fibres. However, as the exothermic curing take place, resin viscosity and temperature of fibre-resin stream increases rapidly. Due to the effect of curing reaction the temperature of fibre-resin stream increases more than the temperature of die. The locations of this peak temperature is defined by the pulling speed of resin-fibre stream through die as shown in Fig. 9.

High pulling speed shifts the peak temperature location toward the end of the die which further increase the pulling force. Although, production rate is increased as pulling speed increases, low degree of cure and poor surface quality would appear. Bibbo [36] developed a theoretical model to calculate the factors which affects the pulling force.

In thermoplastic pultrusion there is no curing reaction of polymer like as in thermoset. Pre-impregnated tapes or prepregs are consolidated and shaped in the die as shown in Fig. 10.

In the die assembly, the control panel is employed to cool the part at controlled rate. Because there is need to control the cooling rate of polymer in die in order to obtain the crystalline part and to achieve the best mechanical properties [37]. Dharia and Schott [35] conducted the study to determine the effect of pull speed and resin viscosity on fibre wet-out. It was noted that the penetration of resin into the fibre yarn or bundle decreases while the coat of roving form outsides increases with increase in pull speed and resin viscosity. It is due to the fact that the penetration at low speed is controlled by capillary forces whereas at high

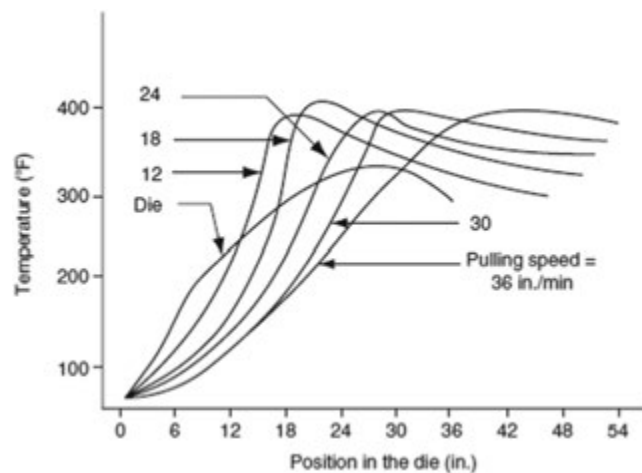


Fig. 9 Temperature distribution at different pulling speeds and along the length of a pultrusion die. Reproduced from Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press. Reproduced from Sumerak, J.E., Martin, J.D., 1986. Applying internal temperature measurement data to pultrusion process control. In: *Proceedings of the 41st Annual Conference, World of Composites: Focus'86*.

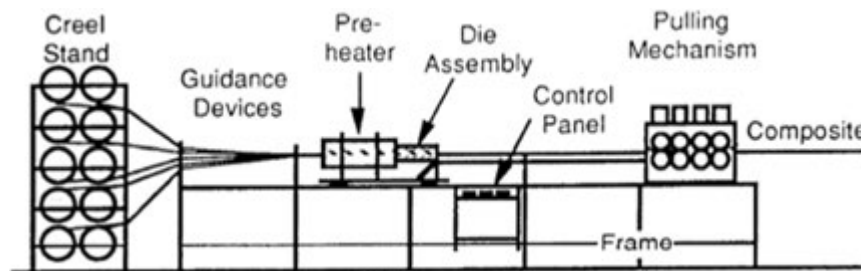


Fig. 10 Thermoplastic pultrusion process. Reproduced from Van de Velde, K., Kiekens, P., 2001. Thermoplastic pultrusion of natural fibre reinforced composites. *Composite structures* 54 (2–3), 355–360.

speed squeeze force is responsible for the same. Chen and Wang [38] investigated the effect of die temperature, pulling rate and fibre content on mechanical properties of glass reinforced polystyrene polymer matrix composite. The mechanical properties improved with increasing the fibre content and die temperature, whereas pulling speed had an inverse effect on mechanical properties of glass/polystyrene composites. Carlsson and Astrom [39] also investigated the effect of pultrusion parameters on properties of glass fibre reinforced polypropylene thermoplastic composites. The process variables such as preheater temperature, cooled die temperature, heated die temperature and pulling speed were varied by using Taguchi method to obtain optimum value of mechanical properties, surface finish, pulling force and fibre distribution over a cross-section.

Fig. 11 (a) and **(b)** shows that fibre distribution is enhanced with decrease in pulling speed and increase in heated die temperature. Flexural strength also improved with increase in heated die temperature. However, preheater temperature put inverse effect on the flexural modulus. Gloss increases with increase in pulling speed, and decrease with increase in preheater temperature as shown in **Fig. 12 (a)** and **(b)**.

Roughness increases with increase in preheater temperature whereas, it decreases with increase in pulling speed as shown in **Fig. 13 (a)** and **(b)**. However, increment in pulling also increases the pulling force which is required to pull the pultruded parts and it leads to the requirement of high power input for the pultrusion process.

Li *et al.* [40] investigated the formation of blister and also investigated the process variables those were responsible for it. The result showed that low temperature of resin and higher pulling speed is responsible for the formation of blister whereas longer dies could help to prevent blister formation.

Filament Winding

Filament winding is a process in which a yarn of resin impregnated fibres is wrapped around a rotating mandrel and then this wrapped mandrel is cured. Applications of filament winding is to produce axisymmetric hollow composites as tanks, pipelines and pressure vessels. **Fig. 14** shows the schematic diagram of filament winding process.

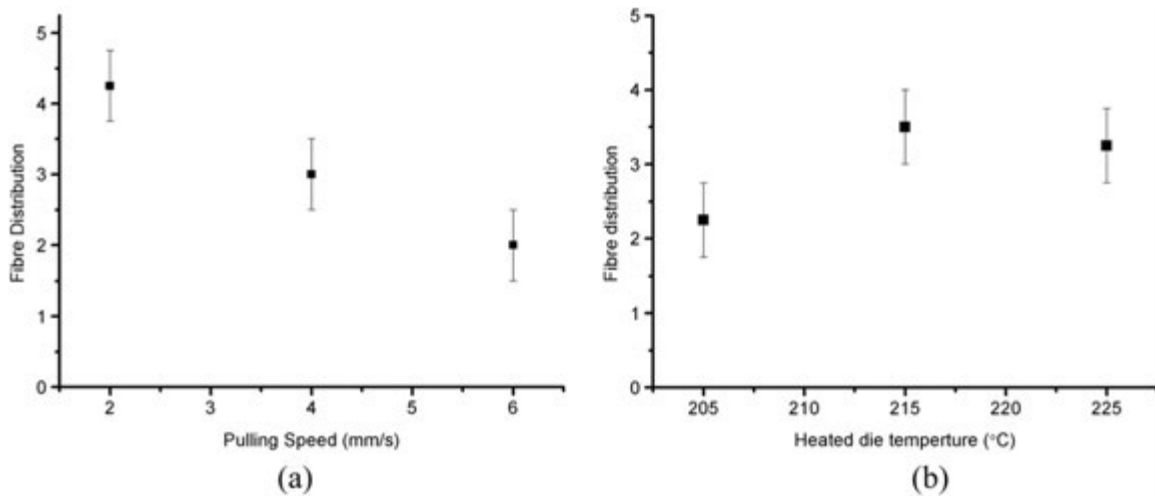


Fig. 11 Fibre distribution versus (a) pulling speed, and (b) heated die temperature. 5 is assigned to well distribute fibres. Reproduced from Carlsson, A., Åström, B.T., 1998. Experimental investigation of pultrusion of glass fibre reinforced polypropylene composites. Composites Part A: Applied Science and Manufacturing 29 (5–6), 585–593.

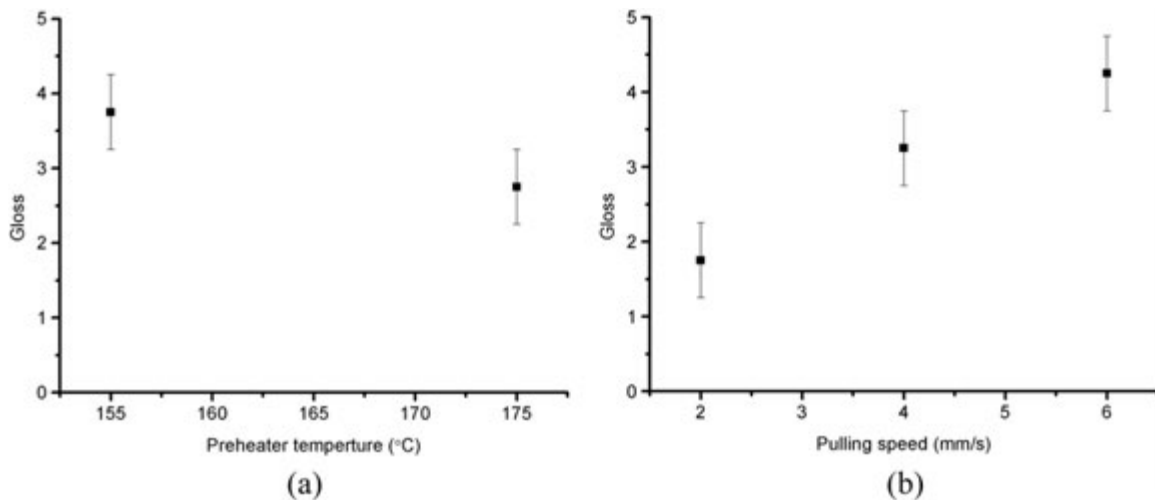


Fig. 12 Gloss versus (a) preheater temperature, and (b) pulling speed. 5 denotes a shiny surface whereas, 1 corresponds to a matt surface. Reproduced from Carlsson, A., Åström, B.T., 1998. Experimental investigation of pultrusion of glass fibre reinforced polypropylene composites. Composites Part A: Applied Science and Manufacturing 29 (5–6), 585–593.

Fibres from a series of creels are pulled into a resin bath for the impregnation. Before to wrap around the rotating mandrel, fibres are gathered into a yarn. The carriage guides the band or yarn while it is going to be wrapped on the mandrel. Wind angle, that is the angle of wrapped yarn with respect to mandrel axis, is generated by the simultaneous control of traverse speed of carriage and rotating speed of mandrel. The gear box is used to control the speed relation between carriage feed and rotational speed of mandrel. Eq. [3] is used to calculate the wind angle.

$$\theta = \frac{2\pi Nr}{v} \quad (3)$$

Where, N is the rotational speed of mandrel per minute, r is the radius of mandrel and v is the carriage feed.

The carriage transverse speed and mandrel rotating speed can also be controlled effectively by using numerical controls in filament winding machines [41]. CNC can be used for filament winding process to produce complex shapes along with high production rate. The required thickness of part could be generated by winding the number of layers over the mandrel. After the winding process the heat is given to mandrel for the completion of curing for thermoset matrix and then the cured part is extracted from mandrel. Resin viscosity, other properties and its processing time is responsible for the voids and delamination defects in the parts produced by filament winding process. The range of viscosity is preferred “between” 1000–2000 cP such that proper wet-out of moving strands could take place. Moreover, the pot life of resin should be higher so that filament winding could be done before

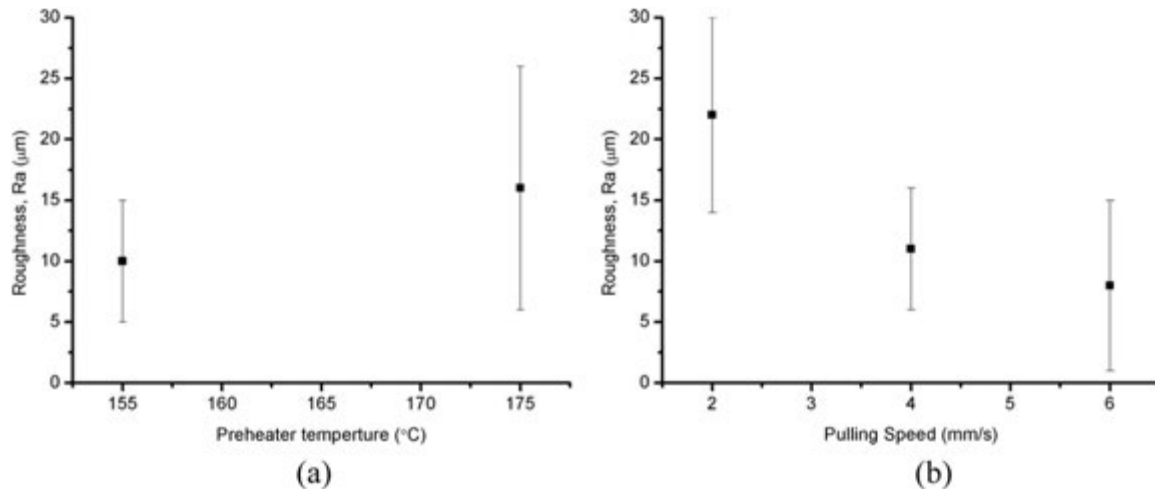


Fig. 13 Roughness versus (a) Preheater temperature, and (b) Pulling speed. Reproduced from Carlsson, A., Åström, B.T., 1998. Experimental investigation of pultrusion of glass fibre reinforced polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 29 (5–6), 585–593.

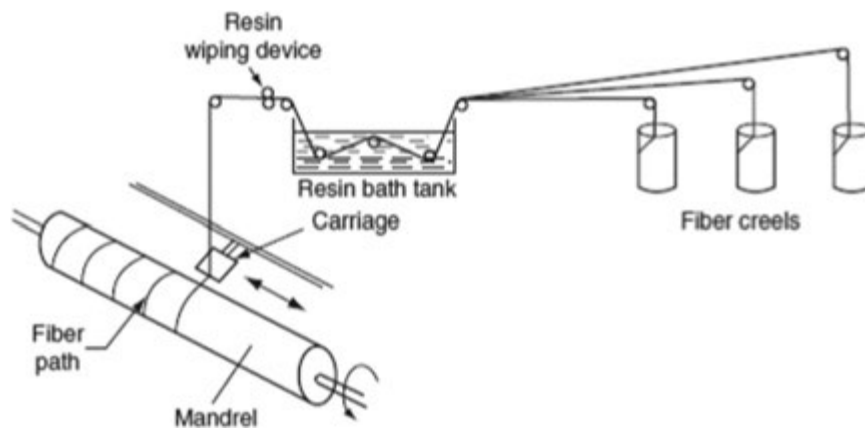


Fig. 14 Schematic diagram of a filament winding process. Reproduced from Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press.

the gelation starts. With the limited pot life of resin, the large parts could take more winding time between two consecutive layers which can result in delamination of final cured part.

High fracture toughness, reparability and weldability are the advantages of thermoplastics over thermoset materials. Owing to these advantages the interest in filament winding of thermoplastics is increasing day by day [42, 43]. Fig. 15 shows the schematic diagram of filament winding process for thermoplastic material.

Fibres are impregnated with the matrix or resin in order to produce part through filament winding [44]. However, the thermoplastic materials do not have curing cycle like as thermosets, only consolidation of thermoplastic is required. Pre-impregnated fibres or tape can be used in this process which have to go through different heating units so that proper consolidation can take place. Moreover, in case of thermoplastic materials the in-situ consolidation that is one step consolidation during winding is possible.

Different to thermoset filament winding process, thermoplastic materials is melted before the impregnation process so that impregnation and consolidation can take place properly. Temperature controls the viscosity of thermoplastic polymer, which is the responsible parameter for the impregnation and consolidation. Along with temperature, the process velocity and consolidation pressure are the important parameters of the filament winding process for thermoplastic materials. Mechanical performance of final part also depends on the winding patterns and crossing points in cross winding [45, 46].

Impregnation of fibres in thermoplastic material is highly time sensitive because of its high viscosity. Thermoplastic materials needs to be heated up more than the melting temperature so that proper impregnation and consolidation can take place. The heat source is the integral part of filament winding process for thermoplastic materials [47]. Schledjewski and Miaris [48] investigated

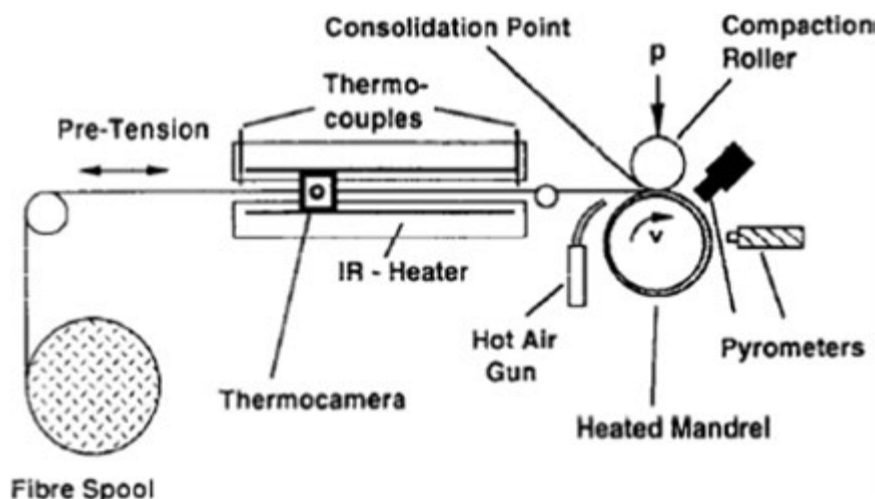


Fig. 15 Schematic diagram of filament winding process for thermoplastic material. Reproduced from Lauke, B., Friedrich, K., 1993. Evaluation of processing parameters of thermoplastic composites fabricated by filament winding. *Composites Manufacturing* 4 (2), 93–101.

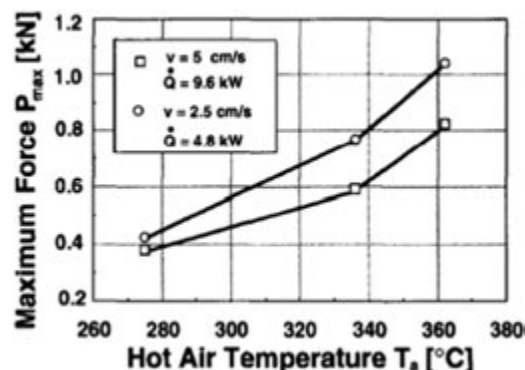


Fig. 16 Maximum force at the nip-point versus hot air temperature, for the two different sources the energy at 100°C mandrel temperature. Reproduced from Lauke, B., Friedrich, K., 1993. Evaluation of processing parameters of thermoplastic composites fabricated by filament winding. *Composites Manufacturing* 4 (2), 93–101.

the parameters to select the heat source for in-situ consolidation of thermoplastic matrix. Beyler *et al.* [49] and Roselli *et al.* [50] have measured the use of laser as heat source for consolidation of thermoplastic tape. However, the effect of hot gas torch [51] and infrared radiation [52] has also been investigated on consolidation as heating methods.

For the consolidation of part, the consolidation roller applies the pressure at the nip point and the temperature of roller is controlled within the range of 60–90°C [53]. Khan *et al.* [54] have also worked to improve the quality and mechanical performance of wound product, and found that adjustable mandrel temperature can help to reduce temperature gradient which leads to improve the quality of final product. Kugler and Moon [55] revealed that by lowering the cooling rate the quality of wound product can be improved further. Lauke and Friedrich [42] investigated the processing parameters of filament winding for manufacturing thermoplastic composites. Consolidation force was calculated by varying nip point temperature, winding speed and IR-heating power. It is clear from Fig. 16 that maximum force was obtained at the highest temperature of hot air and it results in the best consolidation.

At high value of heating power, higher compaction power could be obtained at velocity 10 mm/s and 25 mm/s but not at 50 mm/s. However, at low value of heating power, maximum compaction is quite low even at low winding speed as shown in Fig. 17. The effect of heating power on maximum force can also be estimated from Fig. 18 at mandrel temperature of 100°C.

Compaction force increase up to a particular value of heating power and after then it becomes more or less constant. Because the temperature of impregnated resin, at the end of the preheater, increases with increase in heating power up to its melting temperature after that temperature of resin becomes constant. Similarly, at low heating power the melting temperature could not be obtained and thus, consolidation force decreases. Mertiny and Ellyin [56] studied the influence of filament winding tension on properties of glass-fibre reinforced composite. Mechanical testing was done on the specimens which were manufactured under different winding tension. Results showed that fibre compaction increases with increase in tow tension during filament winding.

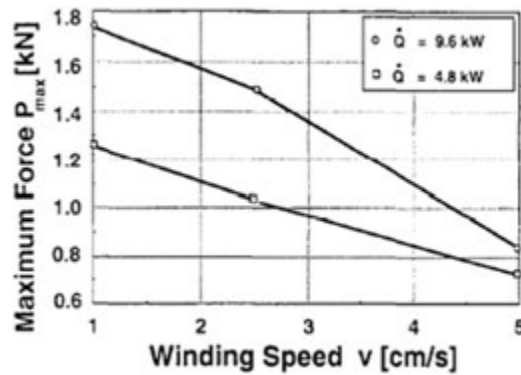


Fig. 17 Maximum axial force versus winding speed at mandrel and hot air temperature 100 and 360°C respectively. Reproduced from Lauke, B., Friedrich, K., 1993. Evaluation of processing parameters of thermoplastic composites fabricated by filament winding. *Composites Manufacturing* 4 (2), 93–101.

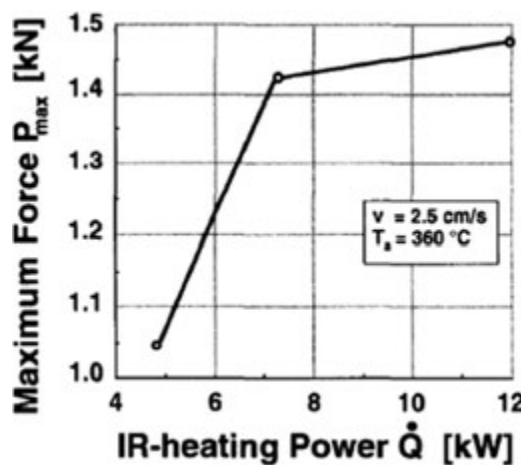


Fig. 18 Maximum axial force versus IR power. Reproduced from Lauke, B., Friedrich, K., 1993. Evaluation of processing parameters of thermoplastic composites fabricated by filament winding. *Composites Manufacturing* 4 (2), 93–101.

Fibre volume fraction was also improved by the high value of tow tension. Mechanical properties of specimens those were manufactured with low and high tow tension, indicated that specimens with tow tension suitable for the fibre dominated applications whereas high tow tension specimens exhibited decrease in the failure strength at matrix dominated applications.

Compression Molding Process

The compression molding technique can produce parts with complex geometry in short time period. Thus, it is suitable for mass production of parts. It is one of the easiest method to produce composite materials as it can transform sheets into final product of the shape of die or mold. This process is used mostly because the scrap is minimum, whereas surface imperfection and waviness defects are still associated with this process. This technique requires the simultaneous control of processing parameters that is pressure, temperature and time. Pressure is required to flow the resin and to remove air bubbles from mold. Whereas, temperature is useful to originate or accelerate the curing reaction. Mallick and Raghupathi [57] discussed the complex heat transfer phenomenon of compression molding process. Fig. 19 shows that surface layer of prepreg approaches the mold temperature and then it is almost same with mold temperature.

Due to low thermal conductivity of fibre, the centreline temperature increases gradually until curing reaction take place at the mid of the prepreg. Owing to the low thermal conductivity of fibres, the heat generated by exothermic curing reaction at the mid of prepreg is not transferred to the top of the surface and eventually centreline temperature increases swiftly to the peak value. Curing of prepreg in compression molding begins at surface and moves inward. However, heat generated by exothermic reaction increase the temperature of the middle of the part and this high temperature may result in the chemical degradation of the resin, hence, high temperature of mold should be avoided.

Among all the defects, blisters are the most commonly occurring defects in compression molding. These are the interlaminar cracks formed due to internal gas pressure as the result of entrapped air between two consecutive layers. Griffith and Shanask [58]

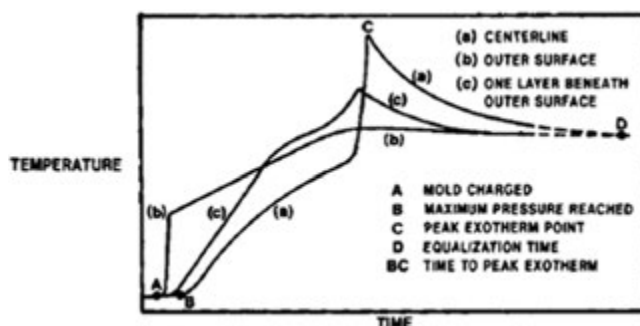


Fig. 19 Representation of temperature-time curves during molding. Mallick, P., Raghupathi, N., 1979. Effect of cure cycle on mechanical properties of thick section fiber-reinforced poly/thermoset moldings. *Polymer Engineering & Science* 19 (11), 774–778.

suggested vacuum molding method to minimize the entrapped air from the mold. Khondker *et al.* [59] used a novel processing technique for manufacturing of jute yarn reinforced thermoplastic matrix composites. Polymer material was braided around the jute yarn to manufacture an intermediate material called microbraid yarn. These microbraid yarns were then wrapped around the metallic plate and this metallic frame was put into compression mold to fabricate unidirectional composites. Mechanical properties of manufactured composites were evaluated. Fibre/Matrix interaction was increased due to improvements in wettability and proper matrix fusion, this interfacial interaction leads to effective stress transfer between fibre and matrix. Hence, the improvement in mechanical properties of microbraid composites can be associated to improvement in wettability of resin into fibre, and interfacial adhesion. Hernandez *et al.* [60] studied the effect of curing cycle on interlaminar shear strength of polymer matrix composites. X-ray micro-tomography was used to determine the effect of curing cycle on void volume and shape. Rheological and thermo-chemical experiments helps to define temperature range for compression molding technique. Specimens were manufactured at different temperatures and 2 bar of pressure. It was found that by increasing the dwell time before gelation helps to reduce void fraction in laminates. Interlaminar shear stress test was conducted for different samples and result show that it decreases with increase in void content. Chani *et al.* [61] analysed the effect of time, temperature and pressure on output. Taguchi method was used to investigate the optimum parameter setting of the compression molding machine. Different levels of parameters considered for the design of experiment are shown in Table 5.

The output responses *i.e.*, tensile and compressive strength for each experimental set are shown in Table 6. It is seen from the table that the tensile and compressive strength are significantly influenced by temperature, pressure and hold duration. The S/N ratio plots shown in Fig. 20 demonstrate the effect of pressure, temperature, and hold duration on the combined response *i.e.*, tensile and compressive strength. The best properties were achieved at pressure of 140 MPa, temperature of 150°C, and hold duration of 30 min.

Resin Transfer Molding (RTM)

In the resin transfer molding process the thermoset resin is injected into a closed mold, where it wet-out the fibres and fills the empty space between fibres. The resin is injected at the lowest point of mold cavity under pressure. Curing of resin is done in mold either at room temperature or at temperature more than room temperature depending upon the type of resin is used. After the curing of part, the mold is dismantled and part is prepared for further secondary operations. RTM is a low pressure process and in comparison to compression molding process it has low tooling cost. It is a cost-effective and labour intensive process, suitable for low to mid volume rate of production.

Thermoset materials are the best choice for the resin transfer molding processes because of low viscosity. Due to low viscosity of thermoset resin, the resistance offered by fibrous perform in the flow of resin is minimum. Hence, the empty space at micron level between the fibres can be filled easily. The viscosity of thermosets lies between 0.1 and 0.5 Pa S, whereas, the same for thermoplastic material varies between 10.2 and 10.6 Pa S. Owing to high viscosity of thermoplastic materials it requires high injection pressure which results into high cost of equipment to be used for RTM processes. Moreover, high injection pressure could displace the fibres and could create resin rich areas which may alter the mechanical properties of final product. Permeability is the important parameter to be considered in RTM process. Although, mechanical properties increases as fibre volume increases, the flow of resin through fibres or the permeability of fibre perform decreases [62, 63]. The modifications in RTM process has been proposed to eliminate the problems of fibre volume fraction and large dimension of the components along with reduction in mold filling time. Chang *et al.* [23] combined the RTM process with compression molding to fabricate fibre reinforced plastic as shown in Fig. 21.

Process variables for this modification were optimized by using Taguchi method to obtain best quality of CRTM products. Compression pressure and resin temperature found to be significant factors for improving the mechanical properties of the part. Whereas, the effect of pre-heated mold temperature was negligible. Low compression pressure and viscosity could help to obtain the part with high quality. Low compression pressure is required in CRTM technology because low compression pressure take more time to be applied, which results in better wetting of fibre perform. Low cycle time, low capital investment and good surface

Table 5 Factors and levels considered in compression molding process

Factor	Levels			
	0	1	2	3
A – Pressure (kN)	100	120	140	160
B – Temperature (°C)	90	120	150	180
C – Hold time (min)	10	20	30	40

Note: Chani, K.S., Saini, J., Bhunia, H., 2018. Effect of nanoclay and bolt preloads on the strength of bolted joints in glass epoxy nanocomposites. Journal of the Brazilian Society of Mechanical Sciences and Engineering 40 (4), 184.

Table 6 Tensile and compressive strength of the laminates cured at different levels of pressure, temperature, and duration

Experimental run	Factor			Tensile strength (MPa)	Compressive strength (MPa)
	A	B	C		
1	0	0	0	349	199
2	0	1	1	368	212
3	0	2	2	377	234
4	0	3	3	378	227
5	1	0	1	368	190
6	1	1	0	377	216
7	1	2	3	390	249
8	1	3	2	390	246
9	2	0	2	377	234
10	2	1	3	390	249
11	2	2	0	390	243
12	2	3	1	395	256
13	3	0	3	377	230
14	3	1	2	390	244
15	3	2	1	395	250
16	3	3	0	390	238

Note: Chani, K.S., Saini, J., Bhunia, H., 2018. Effect of nanoclay and bolt preloads on the strength of bolted joints in glass epoxy nanocomposites. Journal of the Brazilian Society of Mechanical Sciences and Engineering 40 (4), 184.

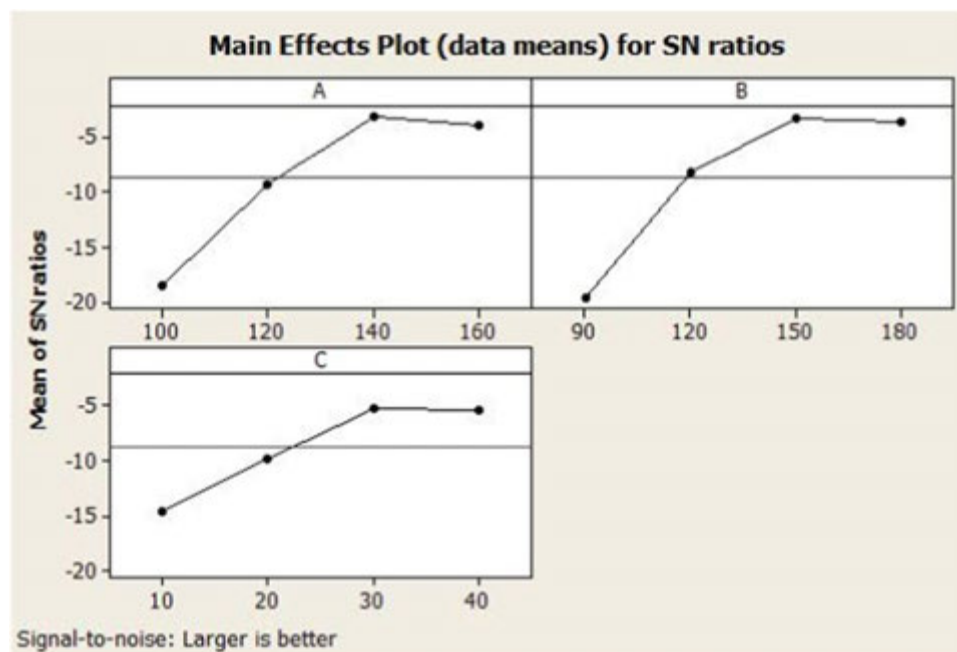


Fig. 20 S/N ratio plots of the combined response of the tensile and the compressive strength of the laminates cured at different levels of a pressure, b temperature, and c duration. Reproduced from Chani, K.S., Saini, J., Bhunia, H., 2018. Effect of nanoclay and bolt preloads on the strength of bolted joints in glass epoxy nanocomposites. Journal of the Brazilian Society of Mechanical Sciences and Engineering 40 (4), 184.

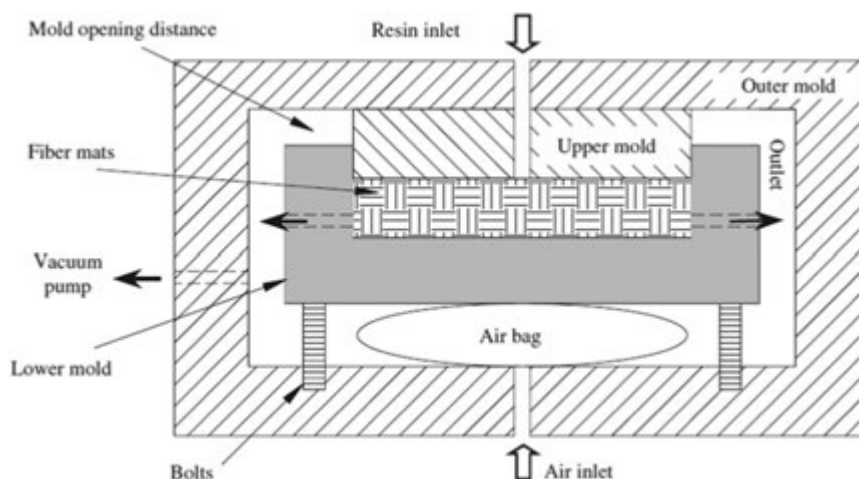


Fig. 21 Schematic diagram of the mold design. Reproduced from Chang, C.-Y., Hourng, L.-W., Chou, T.-Y., 2006. Effect of process variables on the quality of compression resin transfer molding. *Journal of Reinforced Plastics and Composites* 25 (10), 1027–1037.

Table 7 Void content comparison of composites prepared by resin transfer and compression molding techniques

Processing Method	Fibre loading (vol%)	Theoretical density (g/cm ³)	Experimental density (g/cm ³)	Void content (vol%)
Resin transfer molding	19	1.20	1.15	4.16
	27	1.23	1.16	5.69
	43	1.25	1.17	6.40
	50	1.27	1.18	7.08
Compression molding	24	1.21	1.11	8.26
	34	1.24	1.13	8.87
	42	1.26	1.14	9.52
	48	1.29	1.16	10.07

Note: Sreekumar, P., *et al.*, 2007. A comparative study on mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared by resin transfer and compression moulding techniques. *Composites Science and Technology* 67 (3–4), 453–461.

quality part produced by RTM process has made it attractive for manufacturing of automobile components. Sreekumar *et al.* [64] compared the mechanical and physical properties of sisal-leaf fibre reinforced polyester fabricated by compression molding and RTM. **Table 7** shows the void content of parts manufactured by RTM and compression molding at different fibre volume fraction.

Void content increases with increase in fibre volume fraction and it was found to be more in the parts of compression molding technique. Water absorption in a fibrous composite is also due to micro cracks, voids and due to hydrophilic nature of polyester. **Fig. 22** shows mole percentage of water uptake at equilibrium (Q_e) with respect to fibre content.

Neat polymer resin exhibit very low water absorption due to cross linked structure. However, as the fibre volume fraction is increased the water uptake also increases. Along with other factors, tubular structure of fibre increases the water penetration owing to capillary action. Water absorption of composite prepared with RTM technique was also less than that of in compression molding because of good fibre/matrix interaction in RTM. Indira *et al.* [65] also compared the RTM and compression molding techniques for manufacturing the banana-fibre reinforced phenol formaldehyde composites, and results exhibited the same trend in terms of mechanical properties as obtained by Sreekumar *et al.* [64] for two different techniques which were used for manufacturing composites. Papargyris *et al.* [66] used two different heating methods in RTM for processing carbon fibre epoxy composites. Mechanical and physical properties were compared with respect to these methods. It was found that microwave heating process reduces cure cycle, energy requirement and operational cost. In comparison to conventional heating method, microwave heating reduces 50% cure cycle and shows 9% increase in the interlaminar shear strength. Whereas, flexural properties found to be same for normalized common fibre volume fraction.

Careful examination of SEM photographs in **Fig. 23** revealed the poor interfacial bonding and more fibre pull out of parts produced by conventional method than parts produced by microwave heating. **Fig. 24(a)** and **(b)** shows clean fibres in conventionally cured (thermally cured) and fibre coated with significant amount of resin thoroughly for microwave cured parts respectively.

Lee *et al.* [67] measured the effects of glass fibre surface modification on the properties of composite and on the flow characteristics of unsaturated polyester in resin transfer molding process. Glass fibre surface was modified by using γ - MPS treatment, and it was found that permeability of fibre perform decreased because of capillary pressure effect. However, void content in composites with γ - MPS treated glass perform was lower than that of untreated fabric perform, and flexural properties

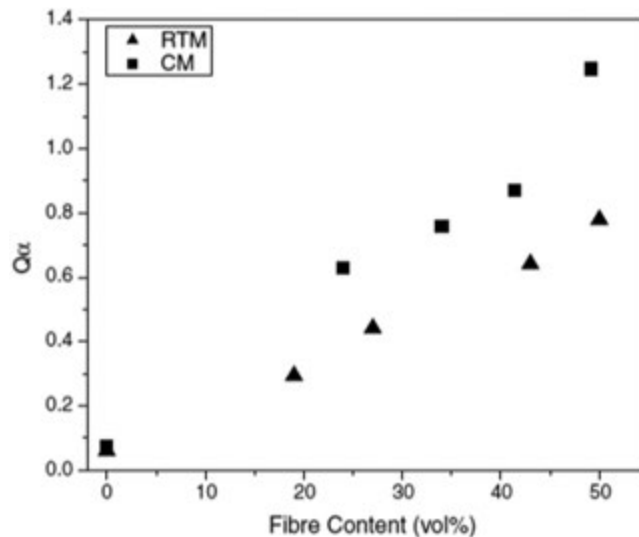


Fig. 22 Comparison of water uptake at 30°C temperature equilibrium. Reproduced from Sreekumar, P., *et al.*, 2007. A comparative study on mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared by resin transfer and compression moulding techniques. *Composites Science and Technology* 67 (3–4), 453–461.

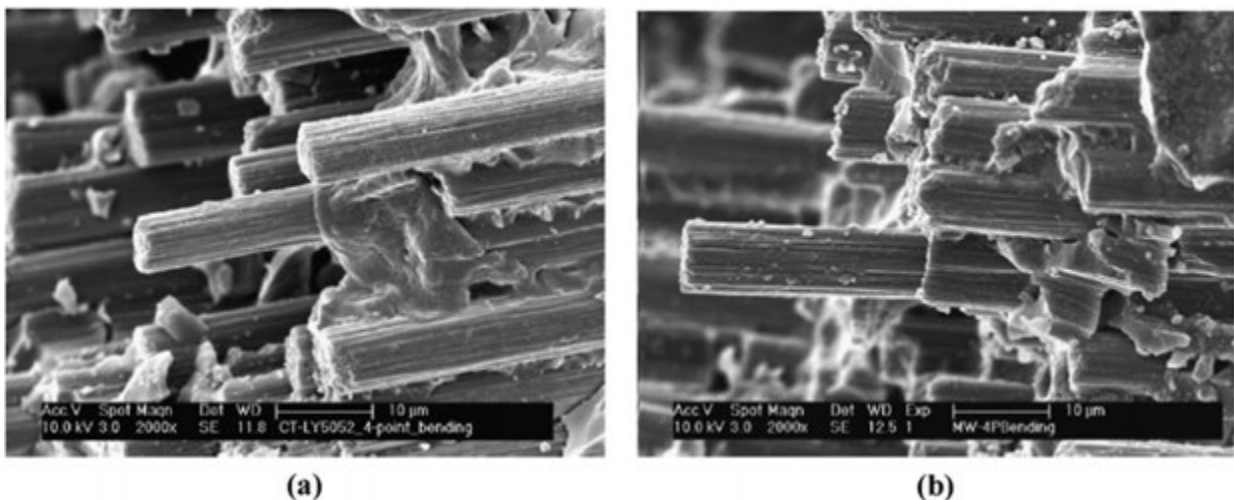


Fig. 23 SEM micrographs showing fibre pull-out after four-point bending test (a) conventionally cured specimen (b) microwave cured specimen. Reproduced from Papargyris, D., *et al.*, 2008. Comparison of the mechanical and physical properties of a carbon fibre epoxy composite manufactured by resin transfer moulding using conventional and microwave heating. *Composites Science and Technology* 68 (7–8), 1854–1861.

of treated glass reinforced composites also improved. High surface quality is required for the part to be used in automotive applications and it is difficult to achieve for RTM technique due to different process and material related issues. Shrinkage during curing of polyester resins make it difficult to obtain high surface finish and part with tight tolerance. Haider *et al.* [68] and Palardy *et al.* [69] used low profile additives (LPA) to reduce cure shrinkage. Taguchi method was used to investigate the effect parameters on the process cycle time and pressure variation, ultimately on surface finish of parts produced by RTM method. Pressure sensors were inserted at various locations of mold cavity to observe pressure during different stages of curing. The minimum cure shrinkage was observed at critical amount of LPA that is at 10%. Due to expansion of LPA, the pressure increases significantly at the later stages of curing. The significant effect of increase in pressure was observed on surface roughness as the surface finish increased with increase in pressure. Injection time and cure gradient found to be decreased with increase in injection pressure. Void is another critical defect which not only effects the surface finish but also uneven void distribution may result in uneven stress distribution. Leclerc and Ruiz [70] conducted the experimental analysis on different fibrous reinforcements to measure the effect of injection parameters of RTM manufacturing on part quality and mechanical performance or ultimately on the macro and micro voids. Based on void measurement and mechanical testing of parts, the relation between void content and their impact on mechanical properties was made and it leads to an optimal value of impregnation velocity. Kaynak *et al.* [71] investigated the

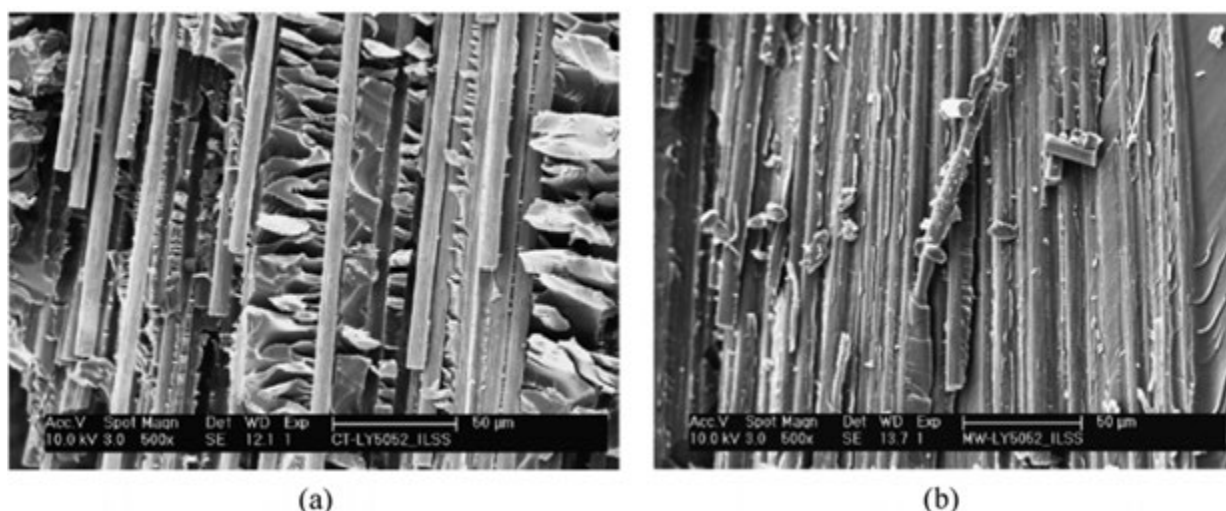


Fig. 24 SEM micrographs after interlaminar shear test showing (a) conventionally cured specimen (b) microwave cured specimen. Reproduced from Papargyris, D., *et al.*, 2008. Comparison of the mechanical and physical properties of a carbon fibre epoxy composite manufactured by resin transfer moulding using conventional and microwave heating. *Composites Science and Technology* 68 (7–8), 1854–1861.

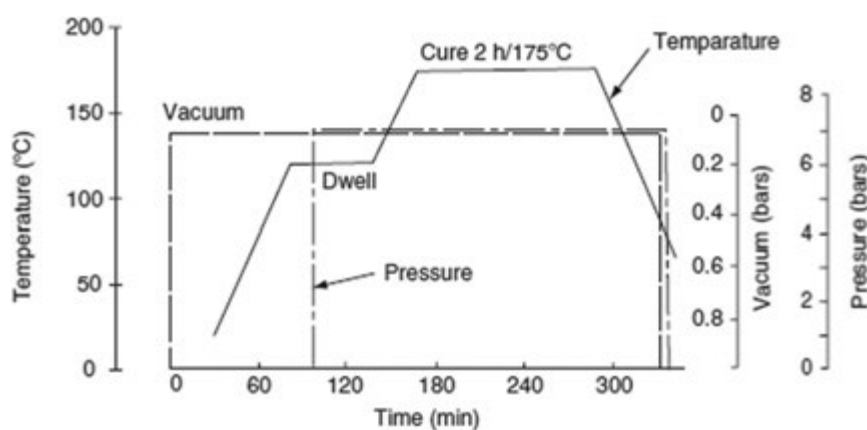


Fig. 25 Typical cure cycle for carbon epoxy prepreg. Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press.

experimental analysis to measure the effect of RTM mold temperature, vacuum and initial resin temperature on the mechanical properties of woven glass epoxy composite. Characterisation of samples was done by ultrasonic C-Scan inspection, thermal analysis, mechanical testing and scanning electron microscopy. Highest mechanical properties were obtained at 60°C temperature of mold with the application of vacuum, and at 28°C initial temperature of resin. Under the application of vacuum the mechanical properties were improved due to decrease in void content in composites. Moreover, mechanical properties are also improved when initial temperature was increased from 15°C to 25°C. Rassmann *et al.* [72] studied the effect of processing conditions of resin transfer molding on mechanical and absorption properties of natural kenaf fibre polyester laminates. At low fibre volume fraction, the tensile and flexural properties increased with increase in mold pressure following injection. However, mold temperature found to be insignificant with respect to impact on mechanical properties.

Bag Molding Process

Bag molding process is used to manufacture polymer based composite materials. The raw material for bag molding process is an uncured prepreg. To convert this raw material into final product the prepreg is heated in an autoclave. Under the effect of temperature, the resin viscosity of partially cured prepreg first decrease up to gel point and then chemical reaction begins and convert the uncured part into final useful product. Fig. 25 shows the typical cure cycle for carbon epoxy prepreg or composite.

After the gel time, the flow of resin from the prepreps decrease significantly. For the proper flow, dwell at temperature lower than the gel time is necessary because it helps to attain uniform temperature throughout and, it gives time to flow resin from prepreg at low viscosity [73]. Fig. 26 shows the effect of dwell time on gelation.

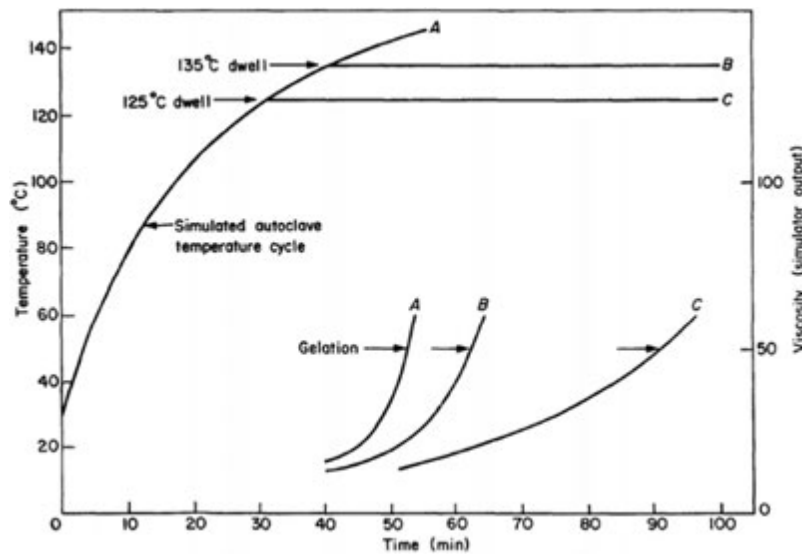


Fig. 26 Effect of dwelling on gel time. Reproduced from Purslow, D., Childs, R., 1986. Autoclave molding of carbon fibre-reinforced epoxies. *Composites* 17 (2), 127–136.

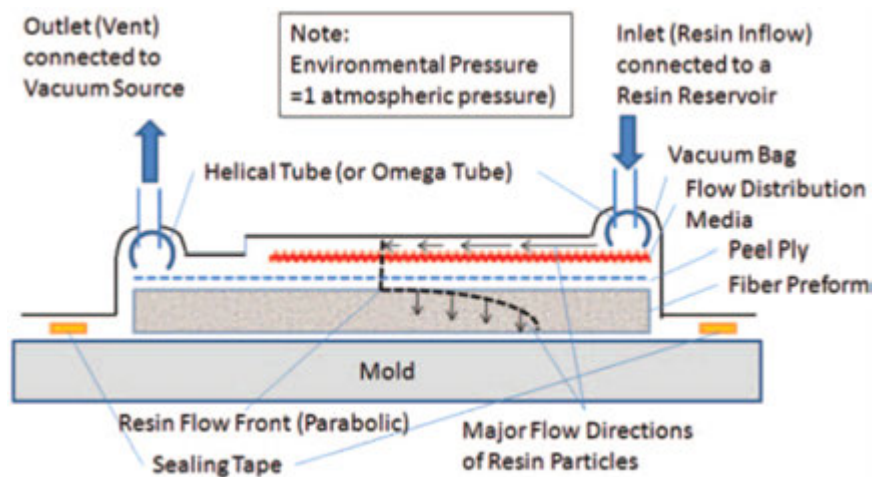


Fig. 27 VARTM process. Reproduced from Kedari, V.R., Farah, B.I., Hsiao, K.-T., 2011. Effects of vacuum pressure, inlet pressure, and mold temperature on the void content, volume fraction of polyester/e-glass fiber composites manufactured with VARTM process. *Journal of composite materials* 45 (26), 2727–2742.

Loss and Springer [74] investigated the thermomechanical behaviour of polymer or resin in a vacuum bag molding process. Experimental study found that cure pressure must be applied just before the gel time so that excess resin could be squeezed out and uniform wetting of prepreg could take place. The cure time required with respect to different cure temperature was also calculated for a particular value of degree of cure in graphite fibre epoxy laminates.

Vacuum-assisted resin transfer molding (VARTM)

Fig. 27 shows a schematic diagram of VARTM process, in which single sided mold is used and sealed with bag for creating vacuum inside a bag. Vacuum not only assists to remove air from mold but also compact the fibres. The resin is drawn into the mold under atmospheric pressure. As the resin infusion take place at atmospheric pressure, the time to fill the mold is very slow in comparison to RTM process [75].

VARTM process is able to manufacture large and complex shapes with high quality. Moreover, it is simple process and can be easily modified for processing different part geometries. All these benefits have made it suitable for marine, aerospace, infrastructure building and defence applications. However, VARTM is not robust as the RTM or autoclave processes. Because compaction pressure on perform or fibres is limited, which eventually leads to low fibre volume fraction in final part.

Gutowski *et al.* [76] established the relation between compaction pressure (P_{comp}) and fibre volume fraction (V_F), which is given as Eq. [4]

$$P_{comp} = A \frac{((V_F/V_{F0}) - 1)}{((1/V_F) - (1/V_{F\infty}))^4} \quad (4)$$

Where, A is the perform spring constant, V_{F0} is the fibre volume fraction at zero compaction pressure and $V_{F\infty}$ is the ultimate fibre volume fraction at infinite compaction pressure. Robitaille and Gauvin [77] introduced another empirical model as Eq. [5]

$$V_F = V_{F1} P_{comp}^B \quad (5)$$

Where, B is the stiffness exponent of fibre perform and V_{F1} is the fibre volume fraction at the unit reference compaction pressure. This model requires only two constants and compaction experiments could help for curve fitting. The thickness (h_2) of composite perform can also be calculated by using fibre volume fraction as per Eq. [6] [78].

$$h_2 = \frac{n_p w_A}{\rho_F V_F} \quad (6)$$

Where, n_p = Number of plies of mats
 w_A = weight per unit area of fibre mat
 ρ_F = Density of fibre material

Permeability is another important factor which affects the resin flow through fibre perform. Kozeny-Carman equation which established relation between permeability (K) and fibre volume fraction is [79] defined as per Eq. [7].

$$K = k \frac{(1 - V_F)^3}{V_F^2} \quad (7)$$

Where, k is a constant, determined from experiments.

Li *et al.* [78] studied relaxation process to reduce compaction variation of fibre perform. In relaxation process enough time is given to mold by closing all gates to distribute compaction uniformly inside the vacuum bag. Compaction relaxation process affects the curing reaction and resin viscosity. More time between the resin filling and curing reaction will allow a complete relaxation process and a more uniform final part. More and more vents could help to accelerate the compaction process [80]. Goren and Atas [81] used PLC as a control unit to control the curing cycle. The vacuum and temperature was controlled by automatic control unit in order to produce void free product with high quality. The advantage of PLC as a control unit is its flexibility to change cure conditions. Void content and fibre volume fraction of a part manufactured by using VARTM process has significant effect on the quality and mechanical properties. Kedari *et al.* [75] investigated the effects of VARTM parameters such as mold temperature, vacuum pressure and inlet pressure on volume fraction and void fraction of glass fibre reinforced polyester composites. Experimental results suggested that fibre volume fraction increases with increase in mold temperature and vent vacuum pressure, due to decrease in resin viscosity. However, void content could increase at higher temperature of mold if injection pressure is not varied accordingly. Although, surface energy of fibres is required more than that of resin, surface energy and viscosity of resin decreases due to increase in temperature of mold or resin [15] which leads to decrease in rise of capillary height of resin, and results in poor wet-out of fibres. However, higher surface energy of fibres leads to strong interfacial bond or more adhesion forces between fibre and matrix. It was concluded that high vacuum, high mold temperature and low inlet pressure can produce a part with low void content and high fibre volume fraction through VARTM process.

The pressure gradient developed during the infusion in VARTM technique and it is responsible for the resin flow into the mold. The resin flow does not stop even after the closer of inlet. This post-filling behaviour disturb the fibre volume fraction and final thickness of cured composite. Simacek *et al.* [80, 82] examined the impact of post-filling flow on fibre volume fraction and thickness of final part. Membrane based VARTM process was used to determine the thickness development during post-infusion. Membrane on the mold acts as a continuous vent during the infusion process and helps to obtain uniform thickness.

Autoclave Process

Autoclave processing is one of the best method for processing laminates with large complexity. By using this technique fibre reinforced plastic composites can be produced for high-performance applications. Autoclave processing technique is very similar to bag molding technique with some modifications [83]. In this technique prepreg are cut into the shape of part to be produced and, then stacked. Then the stacking of prepreps is covered with bleeder and breather in a vacuum bag as shown in Fig. 28.

After filling the resin into the mold the whole assembly is placed into the autoclave where, the pressure and temperature is given to assembly at controlled rate as per curing cycle. At the end of the cycle the cured part is demolded and prepared for further operations. The pressure inside the autoclave is applied to the laminate to consolidate the laminate. The purpose is not only to obtain desired fibre volume fraction but also to remove void formation during cuing cycle.

It is difficult to measure the robustness of autoclave process because a number of parameters are involved in processing. Intelligent process control have been used to minimize the process variations [84–86]. Thermocouples or dielectric sensors has been used to measure autoclave parameters in order to minimize process cycle time as well as temperature gradient of a part during curing [87–90]. Kaushik and Raghavan [91] studied parameters which affect the process-induced warp and reduce the dimensional accuracy of part prepared from thermoset polymer composite during autoclave processing. Static and dynamic

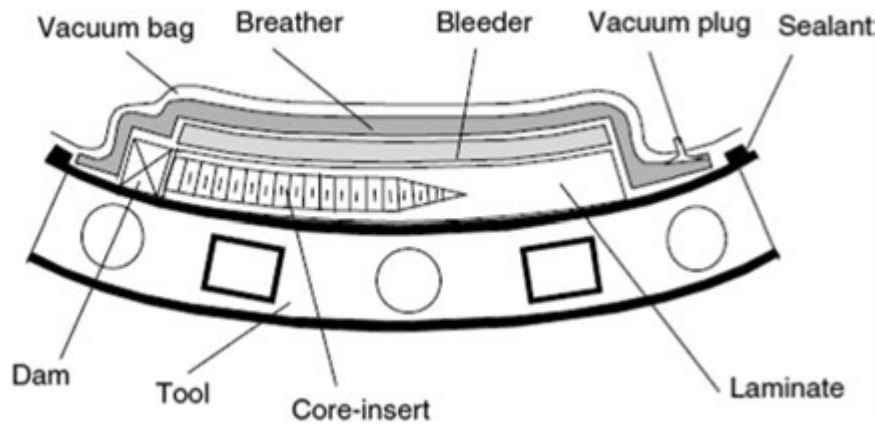


Fig. 28 Tooling prepared for autoclave processing. Reproduced from Advani, S.G., Hsiao, K.-T., 2012. *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. Elsevier.

Table 8 Main characteristics of RTM and autoclaving

Property	RTM	Autoclave
Production output	Moderate (10^2 – 10^5 /annum)	Low (10^1 – 10^2 /annum)
Void content	Low (<2%)	Low (<2%)
Labour intensity	Low-moderate	High
Achievable V_f	Moderate (30%–65%)	High (50%–70%)
Typical applications	Low to medium volume, automobile parts, non-structural components (e.g., automotive spoilers), structural items (e.g., propeller blades, missile boxes)	Aerospace industry, Formula 1 automotive, sporting goods

Note: Abraham, D.S., Matthews, S., McIlhagger, R., 1998. A comparison of physical properties of glass fibre epoxy composites produced by wet lay-up with autoclave consolidation and resin transfer moulding. *Composites Part A: Applied Science and Manufacturing* 29 (7), 795–801.

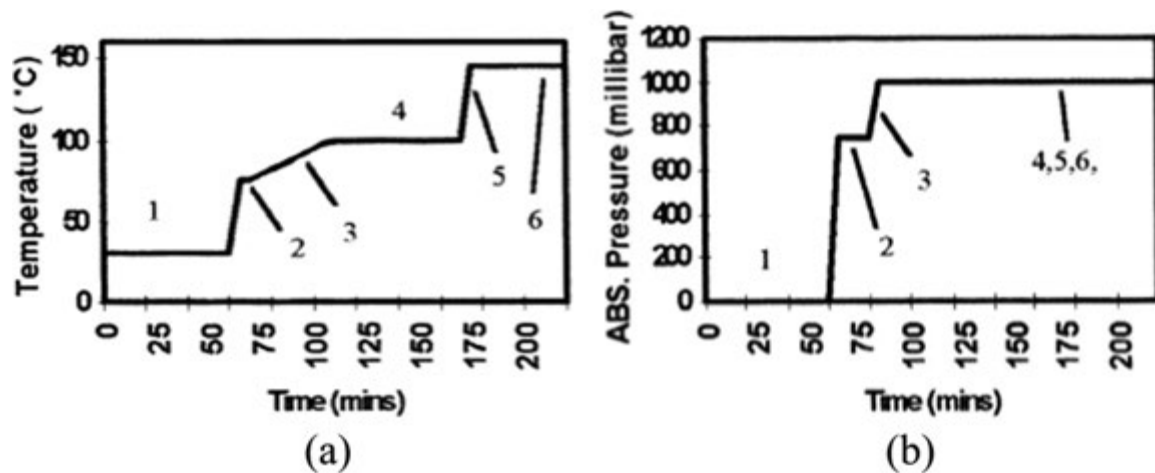


Fig. 29 RTM cure cycle (a) Temperature cycle, (b) Pressure cycle. Reproduced from Abraham, D., Matthews, S., McIlhagger, R., 1998. A comparison of physical properties of glass fibre epoxy composites produced by wet lay-up with autoclave consolidation and resin transfer moulding. *Composites Part A: Applied Science and Manufacturing* 29 (7), 795–801.

frictional coefficients were measured with respect to process time, degree of cure and ramp rate to quantify the tool-part interaction which leads to warpage of composite part. Experimental result shows that both frictional coefficients were maximum at start of cure cycle and changed, as the degree of cure and ramp rate change, due to change in the tool-part interaction. Abraham *et al.* [92] made comparison of properties of glass fibre reinforced epoxy composites manufactured by resin transfer molding and wet-layup with autoclave consolidation. Table 8 summarises the various characteristics of both techniques.

Curing cycle for both the techniques is also different as the number of parameters are different. Figs. 29 and 30 shows the curing cycle for RTM and autoclave processes respectively.

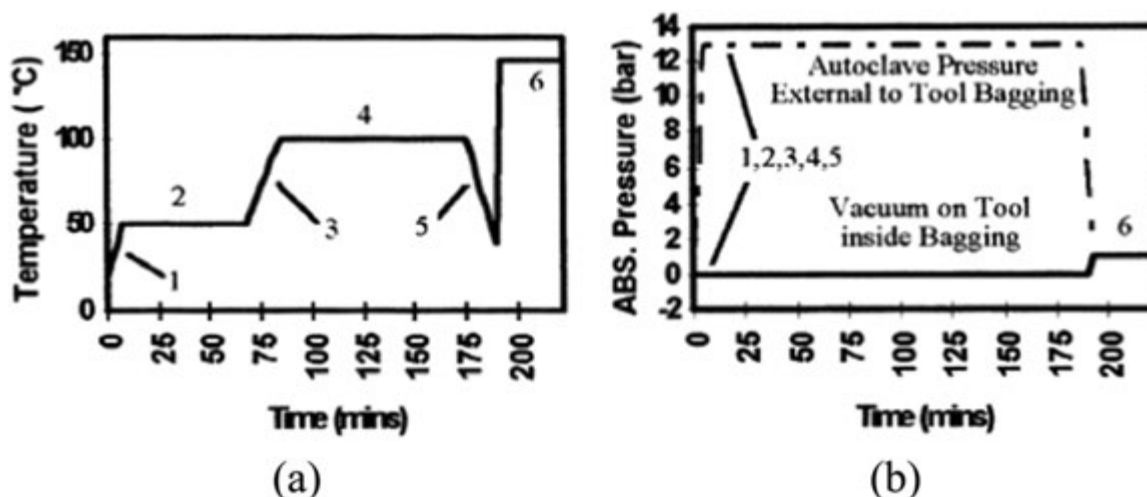


Fig. 30 Autoclave cure cycle (a) Temperature cycle, (b) Pressure cycle. Reproduced from Abraham, D., Matthews, S., McIlhagger, R., 1998. A comparison of physical properties of glass fibre epoxy composites produced by wet lay-up with autoclave consolidation and resin transfer moulding. *Composites Part A: Applied Science and Manufacturing* 29 (7), 795–801.

Table 9 Laminate properties arising from specimens manufactured by wet lay-up with autoclave consolidation and RTM

Property	RTM	Autoclave	RTM % difference
(a) Mechanical Properties			
ILSS (MPa)	17.73 (%CV = 4.9), normalized = 35.16	10.45 (%CV = 2.4), normalized 16.35	+ 69.7%
Flexural strength (MPa)	415.7 (%CV = 3.8), normalized = 824.4	571.2 (%CV = 5.3), normalized = 893.8	– 27.2%
Flexural modulus (GPa)	19.63 (%CV = 3.2), normalized = 38.93	26.43 (%CV = 5.6), normalized = 41.36	– 25.7%
Tensile strength (MPa)	274.0 (%CV = 8.2), normalized = 543.4	332.9 (%CV = 6.6), normalized = 521.0	– 17.7%
Tensile modulus (GPa)	13.91 (%CV = 7.9), normalized = 27.58	16.36 (%CV = 10.5), normalized = 25.60	– 15.0%
Calculated theoretical tensile strength (MPa)	348.3	421.6	– 17.4%
Calculated theoretical tensile modulus (GPa)	19.87	24.61	– 19.3%
(b) Physical properties			
Calculated V_f from mean thickness (%)	50.4	63.9	– 21.1%
Mean thickness (mm)	1.775 (%CV = 4.3)	1.394 (%CV = 2.1)	+ 27.3%
Voidage (%)	1.507 (%CV = 13.4)	1.566 (%CV = 14.1)	– 3.8%
(c) Thermal properties			
T_g (DMA)	145.0 (%CV = 0.4)	1.566 (%CV = 0.6)	– 6.8%
T_g (DSC)	142.9 (%CV = 2.1)	149.9 (%CV = 2.2)	– 4.7%

Note: Abraham, D., Matthews, S., McIlhagger, R., 1998. A comparison of physical properties of glass fibre epoxy composites produced by wet lay-up with autoclave consolidation and resin transfer moulding. *Composites Part A: Applied Science and Manufacturing* 29 (7), 795–801.

In step 1 resin degasses mold under vacuum at 30°C and in step 2 resin is injected into the mold of temperature 75°C at pressure less than atmospheric as shown in Fig. 29. After injection, temperature is raised to 100°C and pressure to atmospheric in step 3. In step 4 composite is cured for 1 hour at identical parameters. 5 and 6 are the post curing parameters of the process.

In step 1 temperature is raised to 50°C and in 2 it dwells for 60 minutes as shown in Fig. 30. After this temperature is raised to 100°C in step 3 and it dwells again in step 4. In step 5 temperature is ramped to 40°C and in step 6 composite is demoulded and post cured.

Results showed that a higher volume fraction could be obtained by using autoclave technology, which leads to higher fibre dominated properties. However, normalized results on the basis of fibre volume fraction for both technique were similar. The matrix dominated properties that is interlaminar shear stress (ILSS) was found to be higher in RTM samples as shown in Table 9.

Manufacturing Processes Particularly for Thermoplastic Polymers

The processing techniques of thermoset materials could also be used for the manufacturing of thermoplastic materials and their composites. However, the thermal behaviour of these two types of polymers is different. The processing temperature for

thermoplastic materials is relatively higher than that of for thermosetting materials. Moreover, in thermoplastic materials no exothermic chemical reaction occurs during the processing. However, working temperature of thermoplastic material is higher than that for thermoset materials and, in the processing of thermoplastic materials and their composites high temperature and pressure is required to consolidate the final part. After consolidation the component is cooled at controlled rate so that residual stresses can be minimized and maximum crystallinity can be attained. Thermoplastic materials can be easily reshaped into useful product under the effect of pressure and temperature. Matched die forming, hydroforming and thermoforming are the basic techniques, which can be used to process thermoplastic materials [93].

Fig. 31 shows matched die forming technique which consists of two matching dies controlled by a hydraulic process. By using this technique a part with a uniform thickness can be formed under pressure. The limitation of producing part with non-uniform thickness can be resolved by using hydroforming. Part with non-uniform thickness can be easily formed by using hydroforming technique.

In hydroforming technique as shown in **Fig. 32**, hydraulically operated diaphragm is used to generate pressure for deforming. Elastomeric diaphragm is installed inside the upper part of mold or die and in the lower part of die, the sheet is to be deformed is placed. The applications of this technique are limited because of the limitations of the elastomeric diaphragm [94].

Thermoforming is another processing technique in which thermoplastic sheets are formed into useful products. **Fig. 33** shows the process diagram of thermoforming. In this technique, the heat is given to sheet in order to increase its temperature up to forming temperature which is slightly higher than the glass transition temperature of thermoplastic. Then preheated sheet is placed in the mold and, vacuum or pressure are applied to mold to form sheet into useful product.

Due to stretching, the polymer sheet undergoes the reduction in its thickness during the thermoforming operation. This reduction leads to a decline in the mechanical properties of formed part. Yang and Hung [95] used the Taguchi method and utility concept to obtain the optimum processing conditions of thermoforming process so that optimum thickness distribution of foam parts can be obtained. Heating temperature, vacuum pressure, plug material, plug speed and plug displacement process parameters were identified to be used in orthogonal array. Vacuum pressure and heating temperature were found to be the most significant factors. Increasing vacuum pressure and heating temperature results in the reduction of the thickness of foamed part.

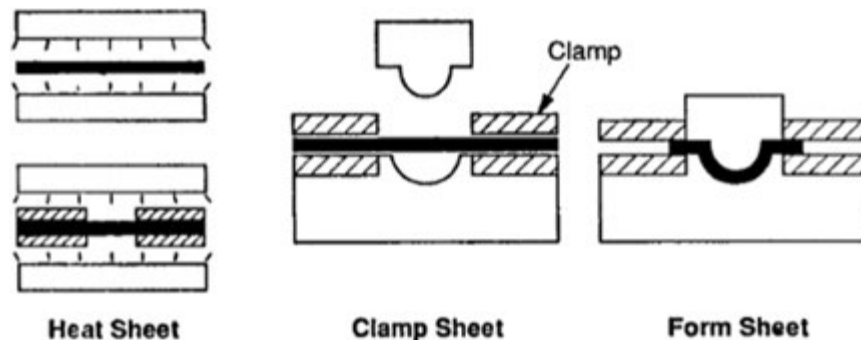


Fig. 31 Schematic process diagram of matched die forming technique. Reproduced from Okine, R.K., 1989. Analysis of forming parts from advanced thermoplastic composite sheet materials. *Journal of Thermoplastic Composite Materials* 2 (1), 50–76.

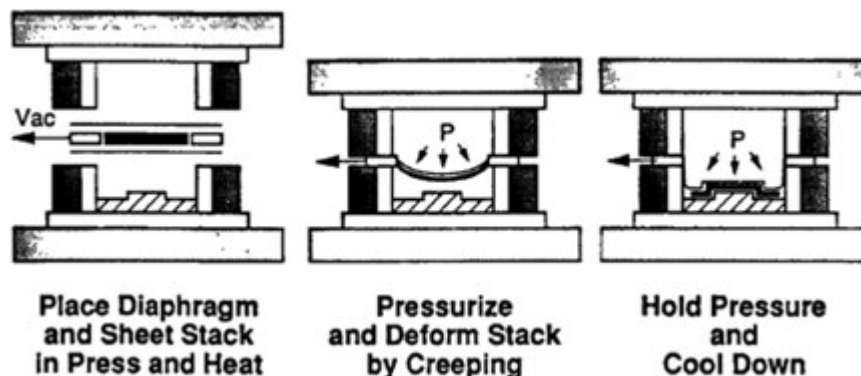


Fig. 32 Process diagram of hydroforming technique. Reproduced from Okine, R.K., 1989. Analysis of forming parts from advanced thermoplastic composite sheet materials. *Journal of Thermoplastic Composite Materials* 2 (1), 50–76. Reproduced from Smiley, A.J., 1988. Diaphragm Forming of Carbon-fibre-reinforced Thermoplastic Composite Materials. Newark, DE (USA): Delaware University.

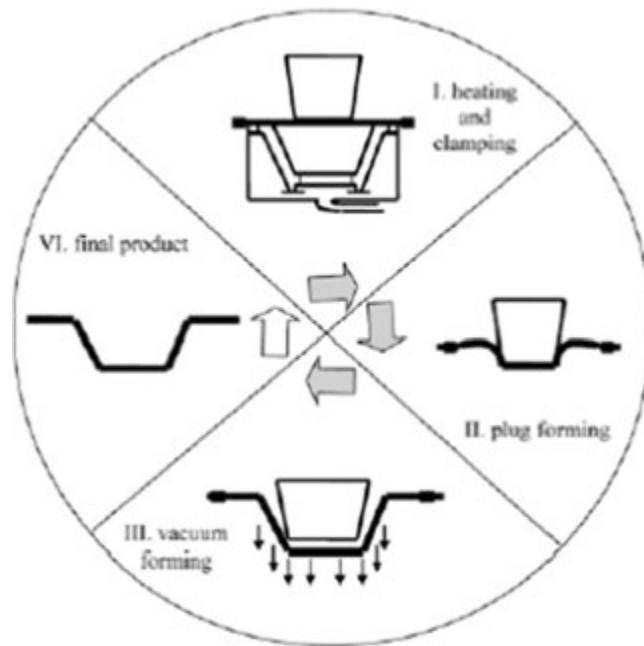


Fig. 33 Schematic of the thermoforming process. Reproduced from Yang, C., Hung, S.-W., 2004. Optimising the thermoforming process of polymeric foams: An approach by using the Taguchi method and the utility concept. *The International Journal of Advanced Manufacturing Technology* 24 (5–6), 353–360.

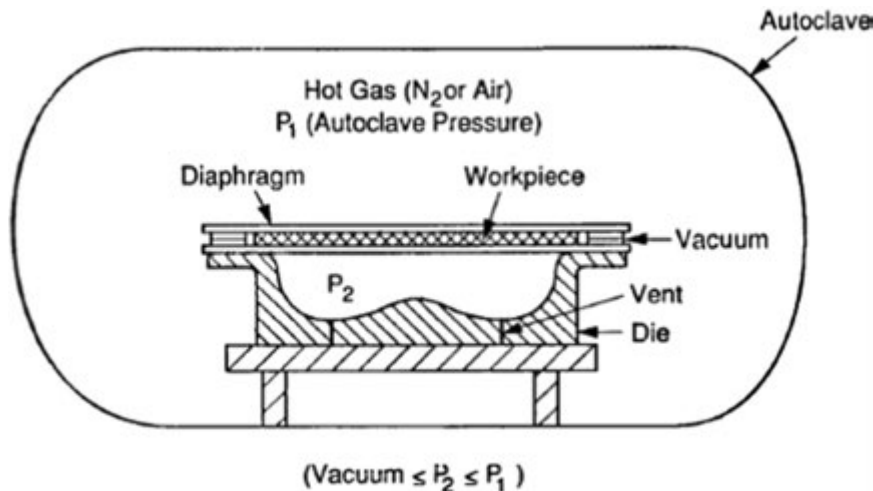


Fig. 34 Schematic of diaphragm forming. Reproduced from Okine, R.K., 1989. Analysis of forming parts from advanced thermoplastic composite sheet materials. *Journal of Thermoplastic Composite Materials* 2 (1), 50–76.

However, thermoforming technique cannot be used to form reinforcing composites as the processing parameters are not suitable to produce it. If this forming technique is applied for thermoplastic matrix composites, it is not possible to stretch laminas without fibre breakage while forming take place. To overcome this problem, the prepreg is placed between deformable diaphragms and the edges of diaphragms are clamped into the die as shown in Fig. 34.

The process cycle for this modification is shown in Fig. 35. This cycle is for carbon fibre reinforced PEEK composite which is processed in autoclave [96].

The temperature of autoclave increased gradually above the melting temperature of PEEK then pressure is applied to consolidate the part. Cogswell [97] have defined the mechanism for the formation of thermoplastic matrix composites as shown in Fig. 36.

In the very first step of flow mechanism, molten polymer flows through the fibres under the effect of pressure called percolation and then fibres start to flow into transverse direction. Percolation and transverse flow of fibres helps to reduce voids, increase consolidation and increase interlaminar adhesion. Along with this intraply shearing and interply slip also take place.

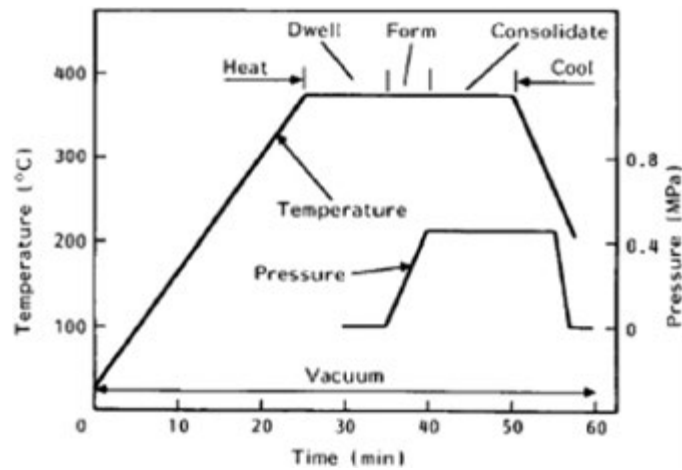


Fig. 35 Process cycle in diaphragm forming. Reproduced from Mallon, P.J., O'Brádaigh, C., Pipes, R., 1989. Polymeric diaphragm forming of complex-curvature thermoplastic composite parts. *Composites* 20 (1), 48–56.

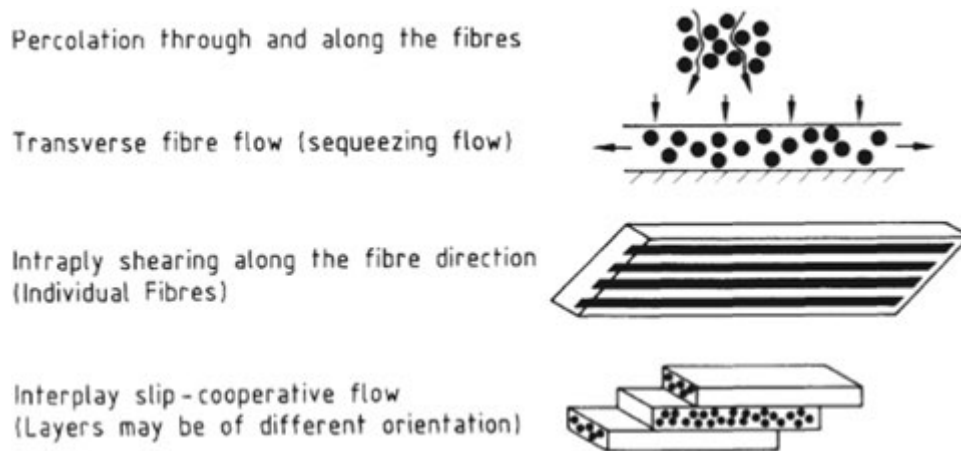


Fig. 36 Flow mechanisms in preimpregnated products. Reproduced from Cogswell, F., 1987. The processing science of thermoplastic structural composites. *International Polymer Processing* 1 (4), 157–165.

Conclusion

The choice of more efficient processing technique to produce parts of polymer as well as its composite materials is important. There could be more than one method to produce a specific part but pros and cons of each process are always associated with it. The following are the conclusions that can be drawn from discussed manufacturing processes.

- (1) Although, degree of cure of thermoset polymer increases with increase in cure time and temperature. However, rate of cure decreases drastically as degree of cure approaches maximum value for a particular temperature. Viscosity of resin increases very rapidly after gel time of thermosets but gel time reduces drastically when curing is done at higher temperature. On the other hand, in case of thermoplastic polymers the material is deformed under the effect of pressure and temperature, after the consolidation deformed part is cooled at controlled rate. Whereas, in case of composites of thermoplastic materials the material is melted and after reinforcement it is consolidated at high pressure and then cooled at controlled rate.
- (2) Injection molding is the cost effective process which can produce parts of complex shapes at high production rate and with high level of precision. In injection molding process the injection velocity is significant parameter for filling the mold to produce parts with complicated geometry. Melt temperature is another prominent parameter to reduce volume shrinkage followed by its pressure. Whereas, short-shot size is the dominated factor in the calculation of water penetration length of water assisted injection molding process.

- (3) Pultrusion is another cost effective method as its cost is approximately 41% of filament winding technique and 26% of hand lay-up technique and it is suitable for producing parts of uniform cross-section area. Die length, temperature and pulling speed are the key parameters of pultrusion process for thermosets to attain maximum degree of cure.
- (4) Filament winding process is used to produce axisymmetric hollow parts. In filament winding process besides the viscosity of resin, high pot life of resin is preferred so that winding can take place before gelation starts. However, in case of thermoplastic the polymer is melted above melting temperature and consolidation force is required for the consolidation of part to make it useful.
- (5) Compression molding process is best for mass production and can produce parts with complex shapes at high production rate. Time, temperature and pressure are the three variables which decide the final properties of manufactured laminate.
- (6) RTM is a labour intensive and cost-effective method for the processing of polymer matrix composites. It is suitable for low to mid volume production rate. It is the best choice for the processing of thermoset matrix composites. Combination of this process with compression molding, known as hybrid technique of manufacturing can improve mechanical properties of final part significantly. However, comparison of RTM and compression molding has proved the RTM process to be best in terms of better physical and mechanical properties of final part.
- (7) In bag molding process the dwell at temperature lower than the gel time is the important step to minimize the defects in part or to maximize the quality of product. Vacuum bag process can be easily modified according to the shape of part to be produced and it is able to produce large and complex shapes of part with high quality. However, compaction pressure on fibre perform in this process is very low. So, this process is not as robust as RTM and autoclave processes. Moreover, mold filling time in this process is high which leads to less production rate in comparison to other processes.
- (8) Although, in comparison to RTM process the labour intensity in autoclave process is high with respect to the production output of both, most of the physical and mechanical properties of part produced by autoclave process are more than that of part of RTM process. Moreover, high fraction of fibre volume fraction can be achieved by autoclave process as compared to RTM process.

References

- [1] Ebeuele, R.O., 2000. *Polymer Science and Technology*. CRC press.
- [2] Hecke, M., Schomburg, W., 2003. Review on micro molding of thermoplastic polymers. *Journal of Micromechanics and Microengineering* 14 (3), R1.
- [3] Friedrich, K., Almajid, A.A., 2013. Manufacturing aspects of advanced polymer composites for automotive applications. *Applied Composite Materials* 20 (2), 107–128.
- [4] Liu, C., Qin, H., Mather, P., 2007. Review of progress in shape-memory polymers. *Journal of Materials Chemistry* 17 (16), 1543–1558.
- [5] Ku, H., *et al.*, 2011. A review on the tensile properties of natural fiber reinforced polymer composites. *Composites Part B: Engineering* 42 (4), 856–873.
- [6] Verrey, J., *et al.*, 2006. Manufacturing cost comparison of thermoplastic and thermoset RTM for an automotive floor pan. *Composites Part A: Applied Science and Manufacturing* 37 (1), 9–22.
- [7] Kootsookos, A., Mouritz, A., 2004. Seawater durability of glass-and carbon-polymer composites. *Composites Science and Technology* 64 (10–11), 1503–1511.
- [8] Liao, [8]K., *et al.*, 1998. Long-term durability of fiber-reinforced polymer-matrix composite materials for infrastructure applications: A review. *Journal of Advanced Materials* 30.
- [9] Sanjay, [9]M., *et al.*, 2016. Applications of natural fibers and its composites: An overview. *Natural Resources* 7 (03), 108.
- [10] Dhandayuthapani, B., *et al.*, 2011. Polymeric scaffolds in tissue engineering application: A review. *International Journal of Polymer Science* 2011.
- [11] Oktem, H., Erzurumlu, T., Uzman, I., 2007. Application of Taguchi optimization technique in determining plastic injection molding process parameters for a thin-shell part. *Materials & design* 28 (4), 1271–1278.
- [12] Landgrebe, D., *et al.*, 2016. Energy-efficiency in a hybrid process of sheet metal forming and polymer injection moulding. *Procedia CIRP* 40, 109–114.
- [13] Guo, Q., *et al.*, 2001. Phase behavior, morphology and interfacial structure in thermoset/thermoplastic elastomer blends of poly (propylene glycol)-type epoxy resin and polystyrene-*b*-polybutadiene. *Polymer* 42 (26), 10101–10110.
- [14] Van de Velde, K., Kiekens, P., 2001. Thermoplastic pultrusion of natural fibre reinforced composites. *Composite Structures* 54 (2–3), 355–360.
- [15] Lee, W.I., Loos, A.C., Springer, G.S., 1982. Heat of reaction, degree of cure, and viscosity of Hercules 3501-6 resin. *Journal of Composite Materials* 16 (6), 510–520.
- [16] Lem, K.W., Han, C.D., 1984. Thermokinetics of unsaturated polyester and vinyl ester resins. *Polymer Engineering & Science* 24 (3), 175–184.
- [17] Han, C.D., Lem, K.W., 1984. Chemorheology of thermosetting resins. IV. The chemorheology and curing kinetics of vinyl ester resin. *Journal of Applied Polymer Science* 29 (5), 1879–1902.
- [18] Mallick, P.K., 2007. *Fiber-Reinforced Composites: Materials, Manufacturing, and Design*. CRC Press.
- [19] Kamal, M.R., 1974. Thermoset characterization for moldability analysis. *Polymer Engineering & Science* 14 (3), 231–239.
- [20] Kamal, M., Sourour, S., 1973. Kinetics and thermal characterization of thermoset cure. *Polymer Engineering & Science* 13 (1), 59–64.
- [21] Gebart, B.R., 1992. Permeability of unidirectional reinforcements for RTM. *Journal of Composite Materials* 26 (8), 1100–1133.
- [22] Hubert, P., Poursartip, A., 1998. A review of flow and compaction modelling relevant to thermoset matrix laminate processing. *Journal of Reinforced Plastics and Composites* 17 (4), 286–318.
- [23] Chang, C.-Y., Hourng, L.-W., Chou, T.-Y., 2006. Effect of process variables on the quality of compression resin transfer molding. *Journal of Reinforced Plastics and Composites* 25 (10), 1027–1037.
- [24] Yang, Y., Gao, F., 2000. Adaptive control of the filling velocity of thermoplastics injection molding. *Control Engineering Practice* 8 (11), 1285–1296.
- [25] Knights, M., 2002. Water injection molding makes hollow parts faster, lighter. *Plastics Technology*. 42.
- [26] Liu, S.-J., Chen, Y.-S., 2004. The manufacturing of thermoplastic composite parts by water-assisted injection-molding technology. *Composites Part A: Applied Science and Manufacturing* 35 (2), 171–180.
- [27] Liu, S.J., Chen, Y.S., 2003. Water-assisted injection molding of thermoplastic materials: Effects of processing parameters. *Polymer Engineering & Science* 43 (11), 1806–1817.
- [28] Song, M., *et al.*, 2007. Research on effects of injection process parameters on the molding process for ultra-thin wall plastic parts. *Journal of Materials Processing Technology* 187, 668–671.
- [29] Ramakrishnan, R., Mao, K., 2017. Minimization of Shrinkage in Injection Molding Process of Acetal Polymer Gear Using Taguchi DOE Optimization and ANOVA Method. *International Journal of Mechanical and Industrial Technology* 4 (2348–7593), 72–79.

- [30] Huang, H.X., Deng, Z.W., 2008. Effects and optimization of processing parameters in water-assisted injection molding. *Journal of Applied Polymer Science* 108 (1), 228–235.
- [31] Mazumdar, S., 2001. *Composites Manufacturing: Materials, Product, and Process Engineering*. CRC Press.
- [32] Sharma, D., *et al.*, 1998. Investigation of dynamic pressure behavior in a pultrusion die. *Journal of Composite Materials* 32 (10), 929–950.
- [33] Sumerak, J.E., Martin J.D., 1986. Applying internal temperature measurement data to pultrusion process control. In: *Proceedings of the 41st Annual Conference, World of Composites: Focus'86*.
- [34] Krolewski, S., Gutowski, T., 1986. Effect of the automation of advanced composite fabrication process on part cost. *SAMPE Q.* 18 (1),
- [35] Dharia, [35]A., Schott, N., 1986. Resin pick-up and fiber wet-out associated with coating and pultrusion processes. *ANTEC* 86, 1321–1325.
- [36] Bibbo, M., 1986. An analysis of the pulling force in pultrusion. *ANTEC* 86, 1430–1432.
- [37] Ahmed, F., Joshi, S.C., Lam, Y., 2004. Three-dimensional FE–NCV modeling of thermoplastic composites pultrusion. *Journal of Thermoplastic Composite Materials* 17 (5), 447–462.
- [38] Chen, C.H., Wang, W.S., 1998. The development of glass fiber reinforced polystyrene for pultrusion. II: Effect of processing parameters for optimizing the process. *Polymer Composites* 19 (4), 423–430.
- [39] Carlsson, A., Åström, B.T., 1998. Experimental investigation of pultrusion of glass fibre reinforced polypropylene composites. *Composites Part A: Applied Science and Manufacturing* 29 (5–6), 585–593.
- [40] Li, J., Lam, Y., Joshi, S.C., 2003. Simultaneous optimization of die-heating and pull-speed in pultrusion of thermosetting composites. *Polymer Composites* 24 (1), 199–209.
- [41] Hermansen, C., Roser R., 1981. Filament winding machine- Which type is best for your application. In: *Proceeding of the 36th Annual Conference of the Reinforced Plastics/Composites Institute*, Washington, DC.
- [42] Lauke, B., Friedrich, K., 1993. Evaluation of processing parameters of thermoplastic composites fabricated by filament winding. *Composites Manufacturing* 4 (2), 93–101.
- [43] Romagna, J., Ziegmann, G., Flemming, M., 1995. Thermoplastic filament winding – An experimental investigation of the on-line consolidation of poly (ether imide) fit preforms. *Composites Manufacturing* 6 (3–4), 205–210.
- [44] Peters, S., Tarnopolskii, Y.M., 1997. Filament winding. In: Mallick, P.K. (Ed.), *Composites Engineering Handbook*. CRC Press, pp. 527–560.
- [45] Paessler, M., Schledjewski, R., 2010. Effect of ring winding technology on NOL ring testing and accompanying characteristics. In: *Proceedings of the European Conference on Composite Materials ECCM*.
- [46] Rousseau, J., Perreux, D., Verdiere, N., 1999. The influence of winding patterns on the damage behaviour of filament-wound pipes. *Composites Science and Technology* 59 (9), 1439–1449.
- [47] Schledjewski, R., 2009. Thermoplastic tape placement process—in situ consolidation is reachable. *Plastics, Rubber and Composites* 38 (9–10), 379–386.
- [48] Schledjewski, R., Miaris, A., 2009. Thermoplastic tape placement by means of diode laser heating. In: *SAMPE-Baltimore*. (MD-18–21 May).
- [49] Beyeler, E., Phillips, W., Güçeri, S.I., 1988. Experimental investigation of laser-assisted thermoplastic tape consolidation. *Journal of Thermoplastic Composite Materials* 1 (1), 107–121.
- [50] Rosselli, F., Santare, M.H., Güçeri, S.I., 1997. Effects of processing on laser assisted thermoplastic tape consolidation. *Composites Part A: Applied Science and Manufacturing* 28 (12), 1023–1033.
- [51] Kim, H.J., Kim, S.K., Lee, W.I., 1996. A study on heat transfer during thermoplastic composite tape lay-up process. *Experimental Thermal and Fluid Science* 13 (4), 408–418.
- [52] Yousefpour, A., Nejhad, M.N.G., 2001. Experimental and computational study of APC-2/AS4 thermoplastic composite C-rings. *Journal of Thermoplastic Composite Materials* 14 (2), 129–145.
- [53] Schledjewski, R., Latrille, M., 2003. Processing of unidirectional fiber reinforced tapes – Fundamentals on the way to a process simulation tool (ProSimFRT). *Composites Science and Technology* 63 (14), 2111–2118.
- [54] Khan, M.A., Mitschang, P., Schledjewski, R., 2010. Identification of some optimal parameters to achieve higher laminate quality through tape placement process. *Advances in Polymer Technology* 29 (2), 98–111.
- [55] Kugler, D., Moon, T.J., 2002. The effects of Mandrel material and tow tension on defects and compressive strength of hoop-wound, on-line consolidated, composite rings. *Composites Part A: Applied Science and Manufacturing* 33 (6), 861–876.
- [56] Mertiny, P., Ellyin, F., 2002. Influence of the filament winding tension on physical and mechanical properties of reinforced composites. *Composites Part A: Applied Science and Manufacturing* 33 (12), 1615–1622.
- [57] Mallick, P., Raghupathi, N., 1979. Effect of cure cycle on mechanical properties of thick section fiber-reinforced poly/thermoset moldings. *Polymer Engineering & Science* 19 (11), 774–778.
- [58] Griffith, R., Shanoski, H., 1977. Reducing blistering in SMC molding. *Plastics Design and Processing*. 10–12.
- [59] Khondker, O., *et al.*, 2006. A novel processing technique for thermoplastic manufacturing of unidirectional composites reinforced with jute yarns. *Composites Part A: Applied Science and Manufacturing* 37 (12), 2274–2284.
- [60] Hernández, S., *et al.*, 2011. Effect of curing cycle on void distribution and interlaminar shear strength in polymer-matrix composites. *Composites Science and Technology* 71 (10), 1331–1341.
- [61] Chani, K.S., Saini, J., Bhunia, H., 2018. Effect of nanoclay and bolt preloads on the strength of bolted joints in glass epoxy nanocomposites. *Journal of the Brazilian Society of Mechanical Sciences and Engineering* 40 (4), 184.
- [62] Bickerton, S., *et al.*, 2000. Fabric structure and mold curvature effects on preform permeability and mold filling in the RTM process. Part I. Experiments. *Composites Part A: Applied Science and Manufacturing* 31 (5), 423–438.
- [63] Han, K., Lee, B., Rice, B., 1998. Permeability measurements of fiber preforms and applications. In: *Proceedings of the 1998 ASME International Mechanical Engineering Congress and Exposition*, Nov. 15. 1998.
- [64] Sreekumar, P., *et al.*, 2007. A comparative study on mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared by resin transfer and compression moulding techniques. *Composites Science and Technology* 67 (3–4), 453–461.
- [65] Indira, K., Parameswaranpillai, J., Thomas, S., 2013. Mechanical properties and failure topography of banana fiber PF macrocomposites fabricated by RTM and CM techniques. *ISRN Polymer Science* 2013.
- [66] Papargyris, D., *et al.*, 2008. Comparison of the mechanical and physical properties of a carbon fibre epoxy composite manufactured by resin transfer moulding using conventional and microwave heating. *Composites Science and Technology* 68 (7–8), 1854–1861.
- [67] Lee, G.-W., *et al.*, 2002. Effects of surface modification on the resin-transfer moulding (RTM) of glass-fibre/unsaturated-polyester composites. *Composites Science and Technology* 62 (1), 9–16.
- [68] Haider, M., Hubert, P., Lessard, L., 2007. An experimental investigation of class A surface finish of composites made by the resin transfer molding process. *Composites Science and Technology* 67 (15–16), 3176–3186.
- [69] Palardy, G., *et al.*, 2008. Optimization of RTM processing parameters for Class A surface finish. *Composites Part B: Engineering* 39 (7–8), 1280–1286.
- [70] Leclerc, J.S., Ruiz, E., 2008. Porosity reduction using optimized flow velocity in Resin Transfer Molding. *Composites Part A: Applied Science and Manufacturing* 39 (12), 1859–1868.
- [71] Kaynak, C., Akgul, E., Isitman, N.A., 2008. Effects of RTM mold temperature and vacuum on the mechanical properties of epoxy/glass fiber composite plates. *Journal of Composite Materials* 42 (15), 1505–1521.

- [72] Rassmann, S., Reid, R., Paskaramoorthy, R., 2010. Effects of processing conditions on the mechanical and water absorption properties of resin transfer moulded kenaf fibre reinforced polyester composite laminates. *Composites Part A: Applied Science and Manufacturing* 41 (11), 1612–1619.
- [73] Purslow, D., Childs, R., 1986. Autoclave moulding of carbon fibre-reinforced epoxies. *Composites* 17 (2), 127–136.
- [74] Loos, A.C., Springer, G.S., 1983. Curing of epoxy matrix composites. *Journal of Composite Materials* 17 (2), 135–169.
- [75] Kedari, V.R., Farah, B.I., Hsiao, K.-T., 2011. Effects of vacuum pressure, inlet pressure, and mold temperature on the void content, volume fraction of polyester/e-glass fiber composites manufactured with VARTM process. *Journal of Composite Materials* 45 (26), 2727–2742.
- [76] Gutowski, T.G., Morigaki, T., Cai, Z., 1987. The consolidation of laminate composites. *Journal of Composite Materials* 21 (2), 172–188.
- [77] Robitaille, F., Gauvin, R., 1998. Compaction of textile reinforcements for composites manufacturing. I: Review of experimental results. *Polymer Composites* 19 (2), 198–216.
- [78] Li, J., *et al.*, 2008. Modeling and analysis of thickness gradient and variations in vacuum-assisted resin transfer molding process. *Polymer Composites* 29 (5), 473–482.
- [79] Correia, [79]N., *et al.*, 2004. Use of resin transfer molding simulation to predict flow, saturation, and compaction in the VARTM process. *Journal of Fluids Engineering* 126 (2), 210–215.
- [80] Simacek, [80]P., *et al.*, 2009. Post-filling flow in vacuum assisted resin transfer molding processes: Theoretical analysis. *Composites Part A: Applied Science and Manufacturing* 40 (6–7), 913–924.
- [81] Goren, A., Atas, C., 2008. Manufacturing of polymer matrix composites using vacuum assisted resin infusion molding. *Archives of Materials Science and Engineering* 34 (2), 117–120.
- [82] Simacek, P., *et al.*, 2012. Experimental validation of post-filling flow in vacuum assisted resin transfer molding processes. *Composites Part A: Applied Science and Manufacturing* 43 (3), 370–380.
- [83] Advani, S.G., Hsiao, K.-T., 2012. *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. Elsevier.
- [84] Holl, M.W., Rehfield, L.W., 1992. An evaluation of the current status of automated process control for thermosetting composites. In: Grimes, G.C. (Ed.), *Composite Materials: Testing and Design* (Tenth Volume). ASTM International.
- [85] Kalra, L., Perry, M.J., Lee, L.J., 1992. Automation of autoclave cure of graphite-epoxy composites. *Journal of Composite Materials* 26 (17), 2567–2584.
- [86] LeClair, S.R., Abrams, F.L., 1988. Qualitative process automation. In: *Proceedings of the 27th IEEE Conference on in Decision and Control*, 1988. IEEE.
- [87] Kenny, J., 1992. Integration of processing models with control and optimization of polymer composites fabrication. In: Advani, S., Blain, W.R., de Wilde, W.P., Gillespie, J.W., Griffin, O.H. (Eds.), *Computer Aided Design in Composite Material Technology III*. Springer, pp. 529–544.
- [88] Kline, R.A., Altan, M.C., 1995. Curing of composite materials using extended heat transfer models. Google Patents.
- [89] Pillai, V., Beris, A.N., Dhurjati, P., 1997. Intelligent curing of thick composites using a knowledge-based system. *Journal of Composite Materials* 31 (1), 22–51.
- [90] Pillai, V.K., Beris, A.N., Dhurjati, P.S., 1994. Implementation of model-based optimal temperature profiles for autoclave curing of composites using a knowledge-based system. *Industrial & Engineering Chemistry Research* 33 (10), 2443–2452.
- [91] Kaushik, V., Raghavan, J., 2010. Experimental study of tool–part interaction during autoclave processing of thermoset polymer composite structures. *Composites Part A: Applied Science and Manufacturing* 41 (9), 1210–1218.
- [92] Abraham, D., Matthews, S., McIlhagger, R., 1998. A comparison of physical properties of glass fibre epoxy composites produced by wet lay-up with autoclave consolidation and resin transfer moulding. *Composites Part A: Applied Science and Manufacturing* 29 (7), 795–801.
- [93] Okine, R.K., 1989. Analysis of forming parts from advanced thermoplastic composite sheet materials. *Journal of Thermoplastic Composite Materials* 2 (1), 50–76.
- [94] Smiley, A.J., 1988. *Diaphragm Forming of Carbon-Fiber-Reinforced Thermoplastic Composite Materials*. Newark, DE: Delaware University.
- [95] Yang, C., Hung, S.-W., 2004. Optimising the thermoforming process of polymeric foams: An approach by using the Taguchi method and the utility concept. *The International Journal of Advanced Manufacturing Technology* 24 (5–6), 353–360.
- [96] Mallon, P.J., O'Brádaigh, C., Pipes, R., 1989. Polymeric diaphragm forming of complex-curvature thermoplastic composite parts. *Composites* 20 (1), 48–56.
- [97] Cogswell, F., 1987. The processing science of thermoplastic structural composites. *International Polymer Processing* 1 (4), 157–165.

Tailored Behavior of Polymer Matrix Composite Materials

Yousef Tamsilian, Samira Alvani, Fatemeh Abdolkhani, and Elham Khademi Moghadam, Shahid Chamran University of Ahvaz, Ahvaz, Iran

© 2021 Elsevier Inc. All rights reserved.

Nomenclature

AlN	Aluminum Nitride	HDPE	High Density Polyethylene
Al ₂ O ₃	Alumina	HNBR	Hydrogenated Nitrile Butadiene Rubber
BN	Boron Nitride	ILSS	Interlayer Shear Strength
CB	Carbon Black	MCF	Milled Carbon Fiber
CF	Carbon Fiber	MEMS	Microelectromechanical Systems
CFRP	Carbon Fiber Reinforced Polymer Composites	MWCO	Molecular Weight Cut-off
CNC	Cellulose Nanocrystal	PCB	Printed Circuit Board
CNT	Carbon Nanotubes	PCM	Structural Polymer Composite Materials
CNTB	Carbon Nanotube Bundle	PEI	Polyetherimide
CTE	Coefficient of Thermal Expansion	PEEK	Polyether Ether Ketone
DC	Direct Current	PMC	Polymer Matrix Composites
DGEBA	Diglycidyl Ether Bisphenol A	PMMA	Polymethyl Methacrylate
DMA	Dynamic Mechanical Analysis	PPS	Polyphenylene Sulfide
FA	Fly Ash	rGO	reduced Graphene Oxide
GNP	Graphene Nanoplatelet	SiC	Silicon Carbide
GNP	Graphene Nanoplatelets	TIM	Thermal Interface Materials
GO	Graphene Oxide	TPE	Carbon Thermoplastic Elastomeric

Introduction

During the last few decades, the use of polymer-based materials in a number of applications has increased very rapidly compared to synthetic materials (Pilla *et al.* 2009a,b; Zhang *et al.*, 2009). Polymers have simplified human lives and influenced every aspect of modern civilization. Today, different kinds of polymers are available from household to aerospace applications and can be easily seen in everyday life (Chalivendra *et al.*, 2003; Gao *et al.*, 2012). Different kinds of materials such as artificial fibers, elastomers, plastics, and polymer composites have been developed using polymers, and these materials are being tailored frequently to meet the desired industrial applications. Polymers have even replaced traditional metals and glass-based materials for a number of applications due to their ease of processing, low cost, and availability (Pinto *et al.*, 2014). However, due to rising environmental awareness, depletion of petroleum resources, and health concerns, the past few years have seen a dramatic shift in the development of novel materials derived from biorenewable resources. Polymer matrix composites (PMCs) are materials that use a polymer-based resin as a matrix material with some form of fibers embedded in the matrix, as reinforcement. Both thermosetting and thermoplastic polymers can be used for the matrix material. Common polymer composite thermosetting matrix materials include polyester, vinyl ester, epoxy, and thermoplastic matrix materials include polyether ether ketone (PEEK), polyetherimide (PEI), polyphenylene sulfide (PPS), polymethyl methacrylate (PMMA). The reinforcements used in such matrices are glass, carbon, and aramid fibers.

This article discusses various tailored behavior of polymer matrix composite materials in order to examine their mechanical, thermal, and electrical properties. The main purpose of this article is to study polymer composites that can meet the specific needs of various engineering applications.

Tailored Behavior Theory

Polymer matrix composite materials are not a new concept, but recent advances have brought many new and exciting composites into existence. By a smart choice of matrix and reinforcement (as well as the best manufacturing process to bring them together) it is possible to make significantly superior materials, with tailored properties for specific applications. In total, tailored behavior theory shows us how to achieve more valuable and practical results by changing some properties of polymer composites.

Thermoset or thermoplastic matrix resins reinforced by fibers are in polymer matrix composites that are much stiffer and stronger than the matrix. Polymer matrix composites are appealing because they are lighter, stronger, and stiffer than the unreinforced polymers or conventional metals, with the additional advantage that their properties and form can be tailored to find the best of a specific application. One of the most common uses of fiber reinforcements is in the military and aerospace industries; this includes carbon fibers and such organic fibers as aramids, liquid crystalline polymers, and ultrahigh-molecular-weight polyethylene. The properties of composite structures depend not only on the fiber reinforcements, but also on the polymer matrix, the characteristics of the interface between the fiber and matrix, and the manufacturing process used to form the finished structure (Park and Seo,

2011). Fiber reinforced polymer composites are also becoming agreeable in modern designs, because of their high specific strength, light weight and ability to be tailored for a specific usage. The development in the commercial and feasible applications of composite materials has motivated researchers to create the next generation of composites. New generation composites purpose to integrate more structural and nonstructural properties into the structure with the aim of enhancing the efficiency of the system as a whole. There have been many endeavors in improving or replacing structural fiber and matrix phases with active materials. Anyway, this methodology generally affects the structural properties of the composite and restricts their practical applications (Malakooti *et al.*, 2017). For example, lightness, durability, strength and ease of production mean that composites will play an increasing part in a boat construction. Despite all the new composites, fiber-reinforced polymer composites are here to stay for many years, though it will undoubtedly be in partnership with other exotic composites. Materials science and composite technology are developing rapidly, and new composites include carbon nanotube and epoxy mixtures. Newly, a small naval vessel with a hull built using carbon nanotubes was delivered as a concept project (Todd, 2020a,b,c). Fiber reinforced polymer composites are often used as structural components that display to extremely high or low heats. Examples such as carbon fiber reinforced polymer composites (CFRP) are lightweight, strong materials used in the manufacturing of innumerable products used in our daily consumption. It is a term used to describe a fiber-reinforced composite material that uses carbon fiber as the primary structural component (Todd, 2020a,b,c).

Dielectric polymer materials with a high dielectric constant and low dielectric loss find many industrial applications such as artificial muscles, energy storage, sensors, flexible electronics, and micro robotics, so it has attracted a lot of attention in the last years. One of the dielectric polymer non-functional cases is the low dielectric constant which was improved by tailoring dielectric properties of polymer composites resulting from controlling alignment of carbon nanotubes (Liu *et al.*, 2016). Also, graphene and its related combinations have been known as wonderful structural nano-fillers that can tailor the properties of new polymer-based composites with particular functionalities. Graphene possesses perfect 2D atomic architecture and has a large surface area that boost the bonding, with tailored functional groups on its surface with polymer chains to form high strength composites. Lately, a lot of researchers have concentrated on developing composites with high specific strength, high electrical and thermal conductivities, high impact resistance, excellent energy storage capability and ability to maintain their strength at low-temperature environments using graphene, graphene oxide (GO), reduced graphene oxide (rGO) or carbon nanotube/graphene. The potentiality of using these materials have been explored for high-tech applications in many researches. Furthermore, it has been demonstrated that the use of graphene-based nanofillers does improve the mechanical, interfacial bonding, electrical, thermal and electromagnetic interference shield properties of polymer-based materials. Appropriately, adding a small amount of these nanofillers can make a big changing in the properties of host materials (Hung *et al.*, 2020).

Flexible and controllable self-regulating heating devices have a great potential for use in applications such as soft robotics, healthcare devices, artificial skins and wearable electronics. Conventional self-regulating heating devices are often limited by the rigid nature of the polymer matrices, particularly at high conductive filler concentrations. Recently, this problem has been successfully answered by binary polymer blends that can achieve a desirable combination of mechanical, electrical and pyroresistive properties. Tailored pyroresistive performance and flexibility by presenting a secondary thermoplastic elastomeric phase into graphene nanoplatelet (GNP) filled polymer composites for self-regulating heating devices (Liu *et al.*, 2018). Now, ultimate goals are to design polymer composites that can meet specific requirements for different engineering applications.

Fabrication Methods of Tailored Polymer-Based Composites

To make the aligned carbon nanotubes/hydrogenated nitrile butadiene rubber (CNT/HNBR) composites, HNBR and carbon nanotube bundle (CNTB) were first mixed using a two-roll mill (Zhanjiang Machinery Factory, China). The gap between the two rolls was adjusted to 0.2 mm for high-shear blending, and the vulcanizer (curing agent, weight ratio of HNBR to vulcanizer of 100:1) was added. The CNTs in the aligned mixture were further aligned by shearing for another 10 min on the two-roll mill with the gap between the two rolls adjusted to the smallest value (<0.1 mm). The optimum curing time was determined with an oscillating disk curemeter, and the composite was vulcanized on a platen presser under 15 MPa at 170 °C. For the random CNT/HNBR composites, the CNT/HNBR mixture was cut into slices with the dimensions of $\sim 5 \times 5 \times 1$ mm³. These slices were then collected into a mold and vulcanized on the platen presser under 15 MPa at 170 °C (Liu *et al.*, 2018). The next method is about using graphene and its associated compounds and there are few issues that should be considered in detail to fabricate (GO)/polymer composites. First item is about degree of uniformity of graphene and its associated components dispersed in polymer composites. Next is purity of nanoparticle received from different sources. The third case is interfacial bonding properties between the nanoparticle and surrounding matrix. And the last case is completely removing all solvents in the solution for dispersing nanoparticle in the nanoparticle/resin solution. So, the structural behavior, reliability, and energy storage capability of graphene reinforced polymer composites at different temperature conditions should be focused to assure they are used safely in different engineering applications (Hung *et al.*, 2020).

Another method for fabricating is about tailoring properties *l*-carrageenan nanocomposites. First, cellulose nanocrystals (CNCs) were synthesized through sulfuric acid-assisted hydrolysis of cellulose according to Iglesias *et al.* (2020). Twenty grams of microcrystalline cellulose were hydrolyzed into a 64 wt% aqueous sulfuric acid solution (400 mL) at 45 °C for 30 min under constant stirring of 300 rpm. The reaction was quenched by adding 20-fold cold distilled water. The suspension was washed via centrifugation at 4000 rpm for 15 min. Colloidal cellulose was then obtained after tip sonication at 40% output for 5 min. The

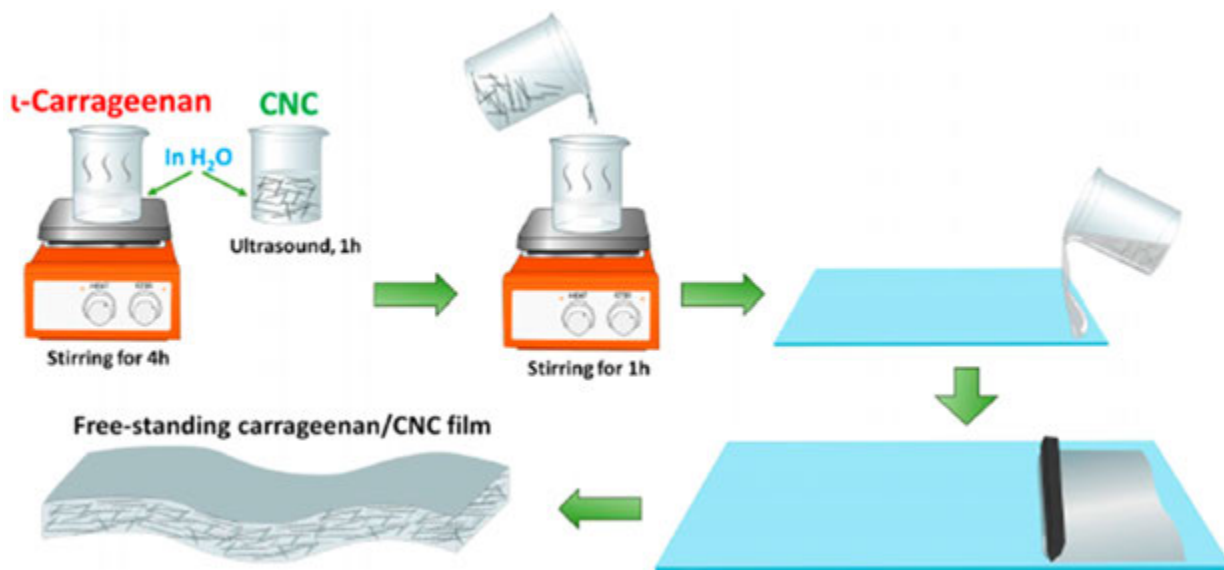


Fig. 1 Schematic diagram depicting ι-carrageenan/CNC nanocomposite film preparation. Adapted from Iglesias, M., Lizundia, E., Costa, C., Lanceros-Méndez, S., 2020. Tailoring electrical and mechanical properties of all-natural polymer composites for environmentally friendlier electronics. *ACS Applied Polymer Materials* 2 (4), 1448–1457.

excess aqueous acid was removed through dialysis for 7 days using a Visking dialysis membrane with a molecular weight cut-off (MWCO) of 12000–14000 Da. Finally, an aqueous CNC dispersion with a pH of 1.9 and a concentration of 1.5 w/w % was obtained. Nanocomposite films were obtained by the doctor-blade technique. First, ι-carrageenan was dissolved in distilled water at 80 °C under a magnetic stirrer for 4 h, whereas CNCs were dispersed in water using an ultrasound bath for 1 h. Then, dispersed CNCs were incorporated into the aqueous ι-carrageenan solution and the resulting mixture was magnetically stirred for 1 h. Finally, single layer films were cast onto clean glass substrates with the aid of a doctor blade (vertically inclined 45°). The process was carried out at a constant rate of approximately 4 cm s^{−1} (equivalent to simple shear rate of 0.6 s^{−1}), where the gap between the blade and substrate was set at 800 μm. The substrate was previously heated at 80 °C with the aim of avoiding a lower solubility of ι-carrageenan arising from a quick cooling of the solution. After room-temperature drying for 24 h, 25 ± 5 μm thick films were obtained (Iglesias *et al.*, 2020) (Fig. 1).

Additives for Tailored Polymer-Based Composites

A much larger dielectric constant than that of polymer composites can be obtained by adding a low content of CNTs to the polymer matrix, with no loss in mechanical properties and processability. One of undesirable properties of CNT/polymer composites is that the large increase in dielectric constant is usually accompanied by an obvious enhancement in dielectric loss, results in largely limiting their applications. Therefore, innovative approaches are required to make dielectric composites with a high dielectric constant and low dielectric loss. One of the common methods to obtain dielectric composites with a high dielectric constant and low dielectric loss is to introduce insulating layers on the surface of CNTs because the insulating layers can effectively stop the direct contact of CNTs with one another. Another way to obtain CNT/polymer dielectric composites with both high dielectric constant and low dielectric loss is to align the CNTs in the polymer matrix, which can reduce the direct connection of CNTs with one another and produce dielectric composites with low direct current (DC) conductivity. The alignment of CNTs in the matrix can be realized by means of electrospinning, microwave curing, liquid crystal-assisted orientation or with the help of external fields like electric, magnetic, and mechanical cases. In particular, the mechanical shearing during traditional mechanical blending can be used to prepare aligned CNT/polymer composites in an industrial scale (Liu *et al.*, 2018).

As mentioned, appropriately adding GO into polymeric matrix could substantially increase the mechanical strength of host polymer materials. Their electrical properties are also improved to prepare the composites more conductive and, further extend their applications to structural capacitors. The GO-coated carbon fiber and carbon fabric have been exhibited strong interfacial bonding properties in composites. Low cost and high effective GO-coated carbon fabric polymer composites demonstrate a great alternative to develop a new generation of carbon fiber (GO/CF) polymer composites (Hung *et al.*, 2020).

The selection of a secondary thermoplastic elastomeric (TPE) phase for adding to a high density polyethylene/graphene nanoplatelets (HDPE/GNP) composites was proved to greatly affect the morphology of the resulting blends, leading to an immiscible binary blend with either a fine or coarse droplet morphology, or a co-continuous morphology, while the location of the conductive nanofiller can be controlled in either one phase or at the interface between two phases (Liu *et al.*, 2018).

Characterizing Tailored Polymer-Based Composites

Composite materials are becoming an inevitable part of our daily lives, as these materials are used for a variety of applications. A better understanding of different properties of composites is very useful in their targeted applications, and therefore the description of composite materials by different techniques plays a major role in the development of durable and high-quality composite products. Polymer-based composite materials provide great flexibility and light weight for the final product. The choice of amplifiers and polymer matrix is crucial in designing a product (Cherusseri *et al.*, 2017).

A composite material is a material that is composed or made of two or more separate phases (matrix phase and dispersed phase), with completely different bulk properties from each of the compounds (Cherusseri *et al.*, 2017). The discontinuous phase is usually harder and stronger than the continuous phase and is called the tailored, while the continuous phase is called the matrix. The matrix holds the reinforcement to create the desired shape while the reinforcement improves the overall mechanical properties of the matrix. Properly covered, it will withstand a great deal of adverse conditions (Deo, 2010). The properties of composites depend on the properties of their constituents, their distribution and the interaction between them. The choice of polymer amplifiers and matrices is essential in designing a product (Cherusseri *et al.*, 2017). The properties of reinforced polymer composites strongly depend on the shape and location of the additive in the matrix. The technology of forming such composites is relatively cheap and easy, in addition, they are suitable for additive-based production. The short CF can be distributed as turbulence in a polymer matrix or it can be oriented. In the latter case, the composites show anisotropy in mechanical, thermal and tribological properties. Among different types of minerals and organics, CFs with relatively low density show the highest tensile strength and elastic modulus. For this reason, CFs, despite their high cost, are widely studied and used. The most promising application of CF is as a reinforcement for polymer-based composites. CF-reinforced polymer composites have been widely used as engineering materials in the aerospace and automotive industries (Chukov *et al.*, 2020).

Various techniques have been used to describe polymer-based composite materials to investigate mechanical, thermal, electrical, magnetic properties, which will be referred to the below sections.

Structural Properties of Reinforced Polymer-Based Composites

Structural polymer-based composite materials (PCMs) are used in different industries: aircraft, missiles, shipbuilding, automotive and electrical industries, construction, sports, chemical and special engineering, medicine, and other applications (Kolosov *et al.*, 2019). This is due to the wide range of physical, mechanical and operational properties of PCM-based materials. For example, such materials combine low density and low modulus of elasticity with high strength and durability and other properties, the shape of the discontinuous phase (which may be allowed by spherical, cylindrical, or rectangular prisms with reciprocal punctures or platelets), and size of the distribution (which controls the texture of the material), and the volume fraction of the interfacial area, all play important role in determining the degree of interaction between the amplifier and matrix. For reinforced applications, structural adhesives should be used. The most common adhesive used in such applications is epoxy due to its excellent adhesion to other materials, but epoxy is brittle. Therefore, by hardening/reinforcing it with other rigid fillers such as carbon nanotubes, fly ash (FA) and milled carbon fiber (MCF), one can mitigate the fragility of the epoxy resin (Kolosov *et al.*, 2019). Recently, CNTs have been used as fillers to increase the strength and values of the composite modulus to enhance the mechanical, physical, and morphological properties of the matrix (Hung *et al.*, 2020).

Structural composites perform excellently in tensile, flexural and impact tests compared to their specimens. Previously, Dutra *et al.* (2000) reported on the performance of a mixture of polypropylene and carbon fibers as reinforcing elements in an epoxy matrix. They discussed the improved properties of hybrids compared to CF-based composites.

Mechanical Properties of Reinforced Polymer-Based Composites

The effects of reinforcement cluster and properties of individual constituents on the overall behavior of the composite under mechanical loading are calculated in terms of effect on elastic modulus and strength. In addition, Chiang *et al.* (2005), Lua (2007), Teodorescu-Draghicescu *et al.* (2009) and Wu (2009) proved that the improvement of mechanical properties has not been successful in all polymer-based composites. The second factors can be considered as an enumerative factor identified, monitored and discussed separately. In material properties testing, flexural strength is usually measured by a 3-point bending test. It has been reported that flexural strength and interlayer shear strength (ILSS) are influenced by the composite design and depend on the position of the reinforcing fiber (Motoc, 2017).

Carbon fiber-based composites have been one of the most appropriate architectures due to some drawbacks of the general reinforcements, including sensitivity to stress concentration due to brittleness, recycling potential and associated production costs. To overcome these weaknesses, the researchers used a combination method with direct cost-benefit and effective properties of materials.

Literatures report on several hybrid/hybrid compounds to be used to exploit the synergistic effects of these compounds among the former. Therefore, Manders and Bader (1981) reported on the flexural properties of carbon fiber and carbon fiber composites. According to their findings, with the relative proportion of carbon fiber decreasing, and with more precise dispersion of carbon fiber, the carbon phase failure pressure increased. They read this behavior as a combined effect and reported an increase in failure pressure of up to 50%. Dynamic mechanical analysis (DMA) is known as a useful tool in studying the behavior of polymer-based composite materials at different temperatures, frequencies or external loading conditions. Measurements can be made using a periodic load to collect the resulting deformation or by applying a fixed load (or a displacement) to obtain creep (or relation) data.

Information on loading modes, calibration methods, sample location, and specific data acquisition can be found in the comprehensive and routine study cited in [Menard \(2008\)](#).

Temperature-dependent dynamic mechanical properties, such as storage modulus, dissipation modulus and mechanical damping (e.g., loss coefficient), allow precise monitoring of the level of interactions (e.g., adhesion) between the polymer matrix and reinforcements. In addition, Cole-Cole or Cole-Davison plots prove to be the most expressive and useful data processing tools in measuring constructive influence. The literature shows a number of sources focusing on fiber-reinforced polymer composites and the properties of their dynamic materials, which show the intrinsic properties of their inherent structure and thermal history during production ([Motoc, 2017](#)). Organic and mineral fibers are considered as high potential reinforcement candidates for various polymer-based composite structures and dynamic mechanical analysis is considered as the most widely used test method to measure the overall behavior of impact and vibration materials. Thermo-mechanical models using temperature-dependent mechanical properties of fiber-reinforced polymer composites were developed around the 1980s. Compression testing of these models has been reported by [Mahieux and Reifsnider \(2001, 2002\)](#). In addition, a Weibull-type function was developed to describe the change in elastic modulus over a range of transfer temperatures. This model is only compatible with thermoplastic materials (e.g., PEEK, PMMA, PPS, etc.) and covers a wide range of temperatures. Other experimental models have been developed by [Gu and Asaro \(2005\)](#). Notably, most researchers have reported on the static and dynamic mechanical properties recovered for their proportional composite specimens. Surprisingly, none of the studies explicitly address the specific issue of similarity between the experimental values recovered from the above configurations, which however, should be the same ([Motoc, 2017](#)).

Thermo-Physical Properties of Reinforced Polymer Based Composite

Uncontrolled thermal expansion in polymer-based composites, especially those designed for structural applications, can cause disturbances that prevent precision of operation in these architectures. To reduce the effects, the constituent can be selected with coefficient of thermal expansion (CTE) at the interfaces or proportionally to vary within a certain range ([Motoc, 2017](#)). References that can be traced in the literatures generally address the issue of thermal expansion in particle-reinforced composites for energy extraction applications, electronic power, electronic packaging, measuring devices, actuators, polymer-based composite architectures for resisting harsh environments ([Motoc, 2017](#)).

Carbon fibers naturally exhibit different CTE responses along their longitudinal and transverse directions and are usually selected as reinforcements for multilayer polymer composite structures to fit their overall CTE. Its fiberglass counterparts, on the other hand, show positive CTE in both longitudinal and transverse directions. By combining “smart” reinforcements, an “ideal” hybrid architecture with zero thermal expansion can be designed. Unfortunately, reality is portrayed beyond these ideal scenarios. Nanoparticles considered as composite structures of polymer particles/composite particles were fabricated and investigated by [Jin and Park \(2012\)](#). In addition to the dynamic and curable mechanical behavior, they controlled the thermal stability of alumina (Al_2O_3) and silicon carbide (SiC) nanoparticles coated with diglycidyl ether bisphenol A (DGEBA) resin, followed by thermal and mechanical properties with increasing the content. Their findings showed that the coefficient of thermal expansion of composite samples in glass and rubber areas decreases with increasing the filler content. Other properties that are studied in the development and description of composite materials are thermal conductivity, especially for various applications such as power electronics, microelectronics, energy storage and storage, sensors and converters and so on ([Alsina et al., 2005](#); [Han and Fina, 2011](#); [Mallik et al., 2011](#); [Otiaba et al., 2011](#)).

Based on the above, a comprehensive work was done by [Lee et al. \(2006\)](#) who investigated various mineral fillers such as aluminum nitride (AlN), wollastonite, whiskers (SiC) and boron nitride (BN) with different shapes and sizes, alone or in combination. Their findings prove the combined effects towards increasing the thermal conductivity due to the advanced connection provided by the filler structure with high aspect ratio. In the next step, the use of larger particles and refined filler surface produce a composite material with increased thermal conductivity. The thermal conductivity of particle-reinforced polymer composites has been extensively studied by [Takei et al. \(1991\)](#), whose theoretical models are among the best predictors of this property of materials. In addition, [Bigg's \(1995\)](#) paper, which extends the above concepts to spherical and irregular fillers, can be studied more comprehensively. In addition, experimental methods, including steady-state and unstable techniques, have been reviewed in the light of heat conduction recovery, especially for applications such as heat exchangers, which are of the primary importance. The thermal conductivity of composite epoxy reinforced composites with particle fillers has been investigated by many researchers, including [Choi and Kim \(2013\)](#) who used aluminum oxide and aluminum nitride fillers, [Teng et al. \(2012\)](#) who addressed this issue using functional multi-walled carbon nanotubes and aluminum nitride or [Zhou et al. \(2010, 2013\)](#) who used hybrid multi-walled carbon nanotube fillers and micro silicon carbide or nano graphite and carbon fillers. [Kandare et al. \(2015\)](#), on the other hand, using recent synergies, reported carbon fiber-based epoxy composites mixed with nanocomposites (e.g., silver and graphene). [Goyal and Balandin \(2012\)](#) also investigated electrically conductive thermal interface materials reinforced with graphene-metal composite fillers. The recovered experimental values showed that graphene fillers are as effective as nanoparticles in increasing thermal properties, and this particular finding is crucial for the thermal management of advanced electronic and optical electronics devices.

[Schuster et al. \(2008\)](#) investigated the thickness and off-plate thermal conductivities of three-dimensional carbon fiber-reinforced polymer composites. Theoretical modeling using finite element method has also been used to increase predictive expressions and their experimental results. In the next step, it can be challenging to consider thermal conductivity as a design aspect with

a diverse fiber architecture that meets mechanical design criteria such as Young's modulus or power. Items listed above were contributed in the shared studies by [Krach and Advani \(1996\)](#), [Kulkarni and Brady \(1997\)](#), [Turias et al. \(2005\)](#). These sources cannot directly address the issue of estimating or predicting effective thermal conductivity, until further developments in this issue are resolved. In general, their aim was to recover the thermal conductivity of polymer-based two-phase composites, reinforced with one-way fibers or mixed, experimentally and theoretically.

Electrical Properties of Reinforced Polymer Based Composite

Because electrical feature is equally important in composite design and applications, and despite the lack of reporting in the literature, knowledge about it has important implications for the optimal design of composites. It is especially important in the construction of functional composites that are structurally different, in that their properties are completely different from those of matrix materials and reinforcements, and they are very different according to the formula of the type of mixed law. Composite materials that have a "coupling" behavior are often referred to as intelligent composites or multipurpose materials ([Motoc, 2017](#)).

First of all, it is necessary to define the meaning of electronic composite, as more broadly defined as a material by [Taya \(2008\)](#): "whose function is primarily to display electromagnetic, thermal and/or mechanical behavior while maintaining structural integrity". Therefore, not only electronic behavior should be examined during studies, but also its physical and pair behavior are required to check. In addition, by referring to the co-authored articles, the developed theoretical models, regardless of the type of amplifiers, shape, size and volume fraction, constitute the deposition mechanism and microscopy. The properties of electronic composites can be tailored to specific applications, such as those in electronic packaging: printed circuit boards (PCBs), thermal interface materials (TIMs), or microelectromechanical systems (MEMS) and BioMEMSs with multiple functions. The intensity of modeling techniques for relaxation processes applied to polymer-based composites can be found. Beyond this shortcoming, [El Hasnaoui et al. \(2014\)](#) randomly dispersed the dielectric properties of epoxy resin matrices with carbon black nanoparticles in varying amounts. The temperature dependence analysis of the electric power using the formulas of Vogel Tammam-Fulcher and Havriliak-Negami showed the existence of carbon black/matrix interaction. Early stages of electronic composite development focus mainly on the use of carbon black (CB) as a conductive filler embedded in a high-density polyethylene matrix ([Vetter et al., 2005](#)) or the combined effect when mixed with carbon fiber in polyethylene mixtures or polyethylene/polypropylene or other polymer matrices ([Motoc et al., 2015](#)).

In addition, the hybrid architecture of particle fibers made from synthetic fibers, including carbon and glass mixed with carbon black, is remarkable. In addition, recent scientific assistance has approached synthetic/natural compounds under the fiber category (e.g., PP/jute blended fabrics) ([Motoc et al., 2015](#)).

Changes in material use patterns and related opportunities along the value chain have made green composites a major topic of intensive research over the past decade. Basically, an insight into the effective dielectric properties of green composite composites is developed. [Jayamani et al. \(2014\)](#) reported on dielectric constant, dissipation coefficient and dielectric loss coefficient of natural jute/bamboo fibers reinforced with composite polypropylene and polyunsaturated composites. In addition, they further argued against the influence of increasing the jute volume fraction on the monitored dielectric properties, in connection with the contribution of the polymer matrix and alkaline treatment of natural fibers.

Potential Applications of Tailored Polymer-Based Composites

These materials have wide strands. About 30% of all custom polymer-based composites produced each year are used in the civil engineering industry. Polymers have good advantages over conventional materials such as light weight, corrosion resistance and ease of processing. They can be combined with fibers to make composites that have reinforced properties, allowing them to be used as members of structures and units. Polymer composites can be found in a variety of forms from structural composites in the construction industry to advanced composites in the aerospace and space satellites industries, as well as in the boating, automotive and rail industries, general engineering, sporting goods, civil engineering, home, and medical applications. Special applications of polymer-based composites include body structure for electric vehicles, wet clutches for torque distribution in car-driven trains and various slip gearboxes, usable space structures, hot-swappable switching, electromagnetic protection, ballistic protection and some other areas. Fiber-reinforced composite materials can have comparable strength to metals and also offer wider range of abilities than metals. The advantages of the polymer (matrix) used for PMC are as follows: obtaining a lightweight material ([Krishna et al., 2016](#)), corrosion resistance, fatigue reduction and good mechanical properties ([Cairns, 2009](#)). The matrix material acts as a fiber alignment as well as a load transformer between the fibers. The strength of the composite increases when using PMC. Matrix material acts as a protection against filler damage ([Crosky, 1991](#)). For this reason, polymer composites have a wide range of applications. Some applications for polymer composites are as follows:

Aircraft is a good example of polymer composites. [Fig. 2](#) shows the polymer composites used in aircraft. These parts include the aircraft frame, protection of the window glass layer (because when the glass is scratched, it increases the risk of breakage and danger to passengers), insulation of electrical parts and aircraft accessories.

Currently, 90% of modern boats are made of PCM, such as fiberglass-reinforced polyester resin. The composition is better both in terms of chemical and mechanical properties of the materials. [Fig. 3](#) shows the boat glass booster and modern polymer fibers used in the structure.



Fig. 2 Fiber-reinforced plastics used in the airplanes (www.pixabay.com).



Fig. 3 Modern boat and polymer fiber glass reinforcement used in the structure (www.pixabay.com).

Fiber-reinforced plastics have been used to reduce earthquake risk in structural applications. The fibers used are either carbon or glass and are used as rods, fabrics, plates and as meshes (Ibraheem and Bandyopadhyay, 2017). Fig. 4 shows how fiber-reinforced plastics have been used in structural applications.

Dental composite is a resin that is reinforced with fillers such as silica, glass and ceramic glasses (Abusallamah, 2010). The reason for using the filler is to improve the wear and fracture resistance of the composite. It is transparent and used for dental cosmetics. A binder such as silane is used to ensure that the filler and resin are completely adhered to each other. Then when the mixture fills the teeth, ultraviolet light should be used to improve the resin composite (Ibraheem and Bandyopadhyay, 2017). Fig. 5 shows a polymer composite used as a filler in dental applications.

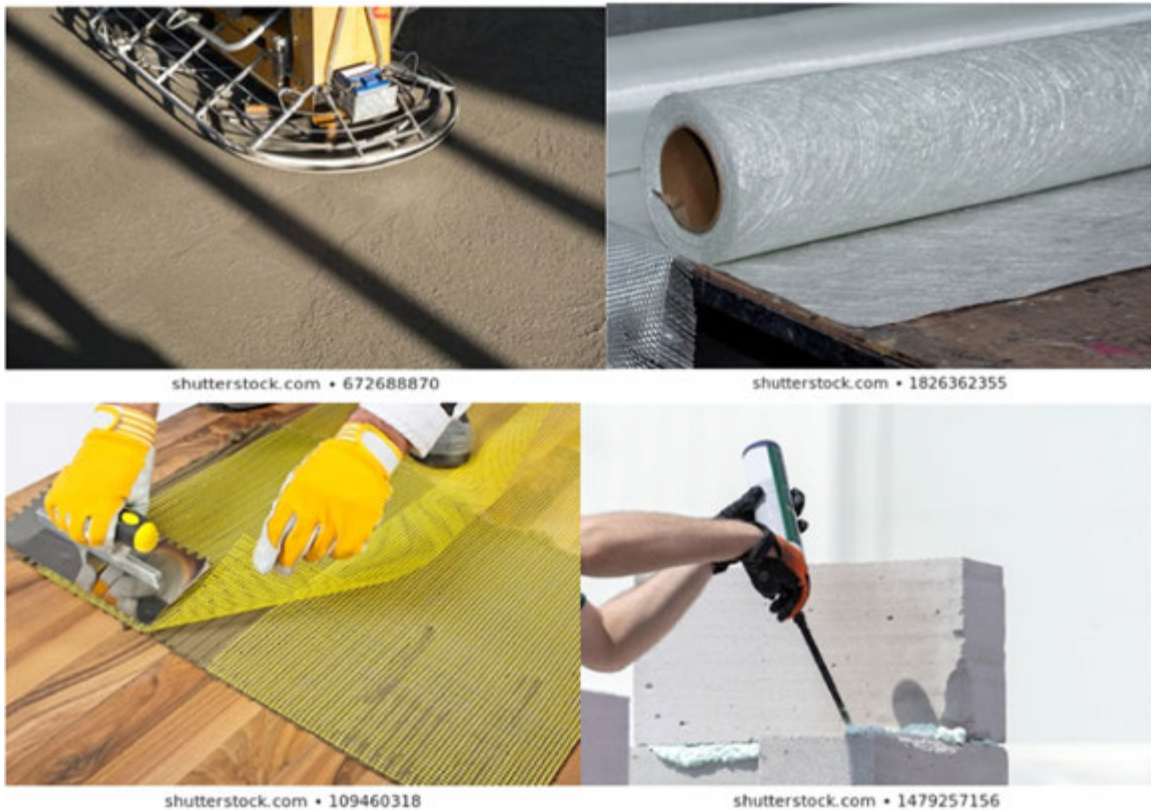


Fig. 4 Different kind of structural applications for the fiber-reinforced polymer (www.shutterstock.com).



Fig. 5 Curing the resin composite by UV light using in dental application (www.pixabay.com).

Natural fiber hybrid composites can be a good alternative to synthetic fiber reinforced composites as structural or semi-structural components, especially in lightweight applications (Sathishkumar *et al.*, 2014; Sanjay and Yogesha, 2017; Yusriah *et al.*, 2014). Replacing synthetic fibers with natural fibers in the today's automotive industry can have economic, environmental and social benefits. This part of the research is still of interest to engineers and experts because natural fiber composites can be an alternative solution to ever-degradable non-renewable sources (Hom *et al.*, 2015; Singleton *et al.*, 2003; Zah *et al.*, 2007). These natural fiber composites have been shown to have better electrical resistance, good mechanical properties, good thermal and acoustic insulation properties, as well as higher fracture toughness (Sanjay *et al.*, 2015; Sanjay and Yogesha, 2016; Yelin *et al.*, 2016). Previously explored industrial applications include window and door frames, furniture, rail beds, car and upholstery panels, gardening equipment, packaging, shelves, aerospace applications, leisure, construction and instrument, and sports. In general, these are items that require very high mechanical strength, but instead reduce purchase and maintenance costs (Faris AL-

Oqila and Sapuan, 2014; Ku *et al.*, 2011). Recent work on natural fiber composites shows that the specific mechanical properties of natural fiber composites are comparable to glass fiber reinforced composites. Natural fiber composites, in the form of panels, tubes, sandwich panels, have been used in the last decade to replace wooden fittings and accessories for furniture and soundproof panels (Alves *et al.*, 2010; Mei-po *et al.*, 2011).

Conclusion and Future Outlooks

Polymer matrix composite materials are not a new innovation, but by recent advances, there are many new tailored composites to existence. Also by smart choice of matrix and reinforcement it is possible to make significantly superior materials, with tailored properties for specific applications. In total, with tailored behavior we can achieve more valuable and practical results by changing some properties of polymer composites. Fiber reinforced polymer composites are becoming more common in industry, because of their high specific strength, light weight and ability to be tailored for a specific usage. Fiber reinforced polymer composites are often used as structural components that have to endure extremely high or low heats. The developments in the commercial and feasible applications of composite materials have motivated researchers to create the next generation of composites. New generation of composites purpose to integrate more structural and nonstructural properties into their structure with the aim of enhancing the efficiency of the system as a whole. Polymers, due to their good advantages over other materials such as low weight, corrosion resistance and ease of processing, can be combined with other fibers and composites with reinforced properties. This property increases the scope of application of such material becomes. The main purpose of production cast is to expand the engineering utilization of advanced polymer matrix composite materials and to increase the applications of polymer composites that are used in a variety of fields, including construction, medicine, aerospace, sailing, automotive and rail, general engineering, and sporting goods. Since its initial release, polymers have had a tremendous impact on the society. People live in a world that is almost impossible to imagine without synthetic polymers. But what is the future of polymer science? In our view, the world of the future is unimaginable without polymers: they make a difference, for example in thermal insulation, fibers and clothing, mobility, building materials, microelectronics, green energy production, soil fertility, food packaging, safety, the search for new antibiotics, regenerative drugs, inkjet-based decentralized construction, lightweight composite materials for windmills and electronic mobility, to explore space, just to name a few from a sheer endless list. This social “market” will occupy us, at least for the foreseeable future, and the polymer industry and related labor market will change, but it will still be fruitful and full of opportunities.

References

- Alsina, O.L.S., De Carvalho, L.H., Ramos Filho, F.G.d., d'Almeida, J.R.M., 2005. Thermal properties of hybrid lignocellulosic fabric-reinforced polyester matrix composites. *Polymer Testing* 24 (1), 81–85.
- Alves, C., Silva, A.J., Reis, L.G., *et al.*, 2010. Eco design of automotive components making use of natural jute fiber composites. *Journal of cleaner production* 18 (4), 313–327.
- Abusallamah, A. 2010. Technique of comopsite resin. Available at: <http://www.slideshare.net/DrAbusallamah/composite-resin-technique?related52>. Dec 13.
- Bigg, D.M., 1995. Thermal conductivity of heterophase polymer compositions. In *Thermal and electrical conductivity of polymer materials*. Berlin Heidelberg: Springer, pp. 1–30.
- Cairns, D.S., 2009. ME 463 Design, Analysis, and Manufacturing Project Fall Semester.
- Chalivendra, V.B., Shukla, A., Bose, A., Parameswaran, V., 2003. Processing and mechanical characterization of lightweight polyurethane composites. *Journal of Materials Science* 38, 1631–1643.
- Cherusseri, J., Pramanik, S., Sowtharya, L., *et al.*, 2017. Polymer-based composite materials: characterizations. *Composite Materials*. 37–77.
- Chiang, M.Y.M., Wang, X., Schultheisz, C.R., He, J., 2005. Prediction and three-dimensional Monte-Carlo simulation for tensile properties of unidirectional hybrid composites. *Composites science and technology* 65 (11–12), 1719–1727.
- Choi, S., Kim, J., 2013. Thermal conductivity of epoxy composites with a binary-particle system of aluminum oxide and aluminum nitride fillers. *Composites Part B: Engineering* 51 (0), 140–147.
- Chukov, D., Nematulloev, S., Tcherdyntsev, V., *et al.*, 2020. Structure and properties of polysulfone filled with modified twill weave carbon fabrics. *Polymer*. 1–17.
- Crosky, A., 1991. UNSW Australia, “polymer composites”. NSW HSC online, engineering studies engineering focus modules aeronautical engineering polymer composites.
- Deo, C.R., 2010. Polymer matrix composite using natural fiber Lantana-Camara.
- Dutra, R.C.L., Soares, B.G., Campos, E.A., Silva, J.L.G., 2000. Hybrid composites based on polypropylene and carbon fiber and epoxy matrix. *Polymer* 41 (10), 3841–3849.
- El Hasnaoui, M., Triki, A., Achour, M.E., Arous, M., 2014. Modelling of dielectric relaxation processes of epoxy-resin filled with carbon black particles. *Physica B: Condensed Matter* 433, 62–66.
- Faris AL-Oqila, M., Sapuan, S.M., 2014. Natural fiber reinforced polymer composites in industrial applications: Feasibility of date palm fibers for sustainable automotive industry. *Journal of Cleaner Production* 6, 347–354.
- Gao, C., Yu, L., Liu, H., Chen, L., 2012. Development of self-reinforced polymer composites. *Progress in Polymer Science* 37, 767–780.
- Goyal, V., Balandin, A.A., 2012. Thermal properties of the hybrid graphene-metal nanomicro-composites: Applications in thermal interface materials. *Applied Physics Letters* 100 (7), 073113.
- Gu, P., Asaro, R.J., 2005. Structural buckling of polymer matrix composites due to reduced stiffness from fire damage. *Composite Structures* 69 (1), 65–75.
- Han, Z., Fina, A., 2011. Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review. *Progress in Polymer Science* 36 (7), 914–944.
- Hom, N.D., Sarasini, F., Santulli, C., *et al.*, 2015. Effect of basalt fiber hybridisation on post-impact mechanical behaviour of hemp fiber reinforced composites. *Compos Part A-Appl. Sci* 75, 54–67.
- Hung, P.Y., Lau, K.T., Guo, Q., Jia, B., Fox, B., 2020. Tailoring specific properties of polymer-based composites by using graphene and its associated compounds. *International Journal of Smart and Nano Materials* 11, 1–17.
- Ibraheem, S., Bandyopadhyay, S., 2017. A review of the structure–property research on hybrid-reinforced polymer composites. *Hybrid Polymer Composite Materials*, 163–191.
- Iglesias, M., Lizundia, E., Costa, C., Lanceros-Méndez, S., 2020. Tailoring electrical and mechanical properties of all-natural polymer composites for environmentally friendlier electronics. *ACS Applied Polymer Materials* 2 (4), 1448–1457.

- Jayamani, E., Hamdan, S., Rahman, M.R., Bakri, M.K.B., 2014. Comparative study of dielectric properties of hybrid natural fiber composites. *Procedia Engineering* 97, 536–544.
- Jin, F.-L., Park, S.-J., 2012. Thermal properties of epoxy resin/filler hybrid composites. *Polymer Degradation and Stability* 97 (11), 2148–2153.
- Kandare, E., Khatibi, A.A., Yoo, S., *et al.*, 2015. Improving the through-thickness thermal and electrical conductivity of carbon fibre/epoxy laminates by exploiting synergy between graphene and silver nano-inclusions. *Composites Part A: Applied Science and Manufacturing* 69, 72–82.
- Katuri, K.P., Bettahalli, N.M.S., Wang, X., *et al.*, 2016. A microfiltration polymer-based hollow-fiber cathode as a promising advanced material for simultaneous recovery of energy and water. *Advanced Materials* 28, 9504–9511.
- Kolosov, A.E., Sivetskii, V.I., Kolosova, E.P., *et al.*, 2019. Creation of structural polymer composite materials for functional application using physicochemical modification. *Advances in Polymer Technology*.
- Krach, A., Advani, S.G., 1996. Influence of void shape, void volume and matrix anisotropy on effective thermal conductivity of a three-phase composite. *Journal of Composite Materials* 30 (8), 933–946.
- Ku, H., Wang, H., Pattarachaiyakoo, N., Trada, M., 2011. A review on the tensile properties of natural fiber reinforced polymer composites. *Compos Part B - Eng.* 42 (4), 856–873.
- Kulkarni, M.R., Brady, R.P., 1997. A model of global thermal conductivity in laminated carbon/carbon composites. *Composites Science and Technology* 57 (3), 277285.
- Lee, G.-W., Park, M., Kim, J., Lee, J.I., Yoon, H.G., 2006. Enhanced thermal conductivity of polymer composites filled with hybrid filler. *Composites Part A: Applied Science and Manufacturing* 37 (5), 727–734.
- Liu, S., Tian, M., Zhang, L., *et al.*, 2016. Tailoring dielectric properties of polymer composites by controlling alignment of carbon nanotubes. *Journal of Materials Science* 51, 2616–2626.
- Liu, Y., Zhang, H., Porwal, H., *et al.*, 2018. Tailored pyroresistive performance and flexibility by introducing a secondary thermoplastic elastomeric phase into graphene nanoplatelet (GNP) filled polymer composites for self-regulating heating devices. *Journal of Materials Chemistry C* 6 (11), 2760–2768.
- Lua, J., 2007. Thermal–mechanical cell model for unbalanced plain weave woven fabric composites. *Composites Part A: Applied Science and Manufacturing* 38 (3), 1019–1037.
- Mahieux, C.A., Reifsnider, K.L., 2001. Property modeling across transition temperatures in polymers: A robust stiffness–temperature model. *Polymer* 42 (7), 3281–3291.
- Mahieux, C.A., Reifsnider, K.L., 2002. Property modeling across transition temperatures in polymers: application to thermoplastic systems. *Journal of Materials Science* 37 (5), 911–920.
- Malakooti, M., Patterson, B., Bowland, C., Hwang, H., Sodano, H., 2017. Piezoelectric interfaces enabled energy harvesting and tailored damping in fiber composites. In: *Proceedings of the SPIE 10172, A Tribute Conference Honoring Daniel Inman*.
- Mallik, S., Ekere, N., Best, C., Bhatti, R., 2011. Investigation of thermal management materials for automotive electronic control units. *Applied Thermal Engineering* 31 (2–3), 355–362.
- Manders, P.W., Bader, M.G., 1981. The strength of hybrid glass/carbon fibre composites. *Journal of Materials Science* 16 (8), 2233–2245.
- Mei-po, H., Wang, H., Lee, J.-H., *et al.*, 2011. Critical factors on manufacturing processes of natural fiber composites. *Composite Part B: Engineering* 43 (8), 3549–3562.
- Menard, K.P., 2008. *Dynamic mechanical analysis: A practical introduction*. 240. CRC Press.
- Motoc, D., 2017. Development of green composites based on epoxidized vegetable oils (EVOs) with hybrid reinforcements: natural and inorganic fibers.
- Motoc, D.L., Bou, S.F., Gimeno, R.B., 2015. Effects of fibre orientation and content on the mechanical, dynamic mechanical and thermal expansion properties of multi-layered glass/carbon fibre-reinforced polymer composites. *Journal of Composite Materials* 49 (10), 1211–1221.
- Otiaba, K.C., Ekere, N.N., Bhatti, R.S., *et al.*, 2011. Thermal interface materials for automotive electronic control unit: Trends, technology and R&D challenges. *Microelectronics Reliability* 51 (12), 2031–2043.
- Park, S., Seo, M., 2011. Chapter 7 – Types of composites. *Interface Science and Technology*. Elsevier.
- Pilla, S., Gong, S., O'Neill, E., Yang, L., Rowell, R.M., 2009a. Polylactide-recycled wood fiber composites. *Journal of Applied Polymer Science* 111 (1), 37–47.
- Pilla, S., Kramschuster, A., Yang, L., *et al.*, 2009b. Microcellular injection-molding of polylactide with chain-extender. *Materials Science and Engineering: C* 29 (4), 1258–1265.
- Pinto, M.A., Chalivendra, V.B., Kim, Y.K., Lewis, A.F., 2014. Evaluation of surface treatment and fabrication methods for jute fiber/ epoxy laminar composites. *Polymer Composites* 35, 310–317.
- Sanjay, M.R., Yogesha, B., 2016. Study on water absorption behaviour of jute and kenaf fabric reinforced epoxy composites: Hybridization effect of E-glass fabric. *International Journal of Composite Materials* 6 (2), 55–62.
- Sanjay, M.R., Yogesha, B., 2017. Studies on natural/glass fiber reinforced polymer hybrid composites: An evolution. *Materials today: Proceedings* 4 (2), 2739–2747.
- Sanjay, M.R., Arpitha, G.R., Yogesha, B., 2015. Study on mechanical properties of natural-glass fibre reinforced polymer hybrid composites: A review. *Materials today: Proceedings* 2 (4–5), 2959–2967.
- Sathishkumar, T.P., Navaneethakrishnan, P., Shankar, S., Rajasekar, R., 2014. Mechanical properties and water absorption of short snake grass fiber reinforced isophthalic polyester composites. *Fibers and Polymers* 15 (9), 1927–1934.
- Schuster, J., Heider, D., Sharp, K., Glowania, M., 2008. Thermal conductivities of three-dimensionally woven fabric composites. *Composites science and technology* 68 (9), 2085–2091.
- Singleton, A.C.N., Baillie, C.A., Beaumont, P.W.R., Peijs, T., 2003. On the mechanical properties, deformation and fracture of a natural fibre/recycled polymer composite. *Composites Part B: Engineering* 34 (6), 519–526.
- Takei, T., Hatta, H., Taya, M., 1991. Thermal expansion behavior of particulate-filled composites II: Multi-reinforcing phases (hybrid composites). *Materials Science and Engineering: A* 131 (1), 145–152.
- Taya, M., 2008. *Electronic composites. modeling, characterization, processing, and MEMS Applications*. Cambridge University Press.
- Teng, C.-C., *et al.*, 2012. Synergetic effect of thermal conductive properties of epoxy composites containing functionalized multi-walled carbon nanotubes and aluminum nitride. *Composites Part B: Engineering* 43 (2), 265–271.
- Teodorescu-Draghicescu, H., Vlase, S., Chiru, A., Scutaru, M.L., Motoc, D.L., 2009. On the elastic constants of a fibre-reinforced composite laminate. In: *Mastorakis, N.E., Martin, O., Zheng, X.J. (Eds.), Proceedings of the 2nd WSEAS International Conference on Engineering Mechanics, Structures and Engineering Geology*. pp. 155–158.
- Todd, J., 2020a. A list of composite materials in boats. *ThoughtCo.* (thoughtco.com/composite-materials-in-boats-820410).
- Todd, J., 2020b. Thermal properties of composites. *ThoughtCo.* (thoughtco.com/thermal-properties-of-composites-820516).
- Todd, J., 2020c. Understanding CFRP composites. *ThoughtCo.* (thoughtco.com/understanding-cfrp-composites-820393).
- Turias, I.J., Gutiérrez, J.M., Galindo, P.L., 2005. Modelling the effective thermal conductivity of an unidirectional composite by the use of artificial neural networks. *Composites Science and Technology* 65 (3–4), 609–619.
- Vetter, J., Novák, P., Wagner, M.R., *et al.*, 2005. Ageing mechanisms in lithium-ion batteries. *Journal of power sources* 147 (1–2), 269–281.
- Wu, Z., 2009. Three-dimensional exact modeling of geometric and mechanical properties of woven composites. *Acta Mechanica Solida Sinica* 22 (5), 479–486.
- Yelin, D., Dimos, P., Yajun, T., *et al.*, 2016. Life cycle assessment of flax-fiber reinforced epoxidized linseed oil composite with a flame retardant for electronic applications. *Journal of Cleaner Production* 133, 427–438.
- Yusriah, L., Sapuan, S.M., Zainudin, E.S., Mariatti, M., 2014. Characterization of physical, mechanical, thermal and morphological properties of agro-waste betel nut (*Areca catechu*) husk fibre. *Journal of cleaner production* 72, 174–180.
- Zah, R., Hirschier, R., Leão, A.L., Braun, I., 2007. Curauá fibers in the automobile industry—a sustainability assessment. *Journal of cleaner production* 15 (11–12), 1032–1040.
- Zhang, C., Subramanian, H., Graier, J.J., *et al.*, 2009. Fabrication of biodegradable poly (trimethylene carbonate) networks for potential tissue engineering scaffold applications. *Polymers for Advanced Technologies* 20 (9), 742–747.

- Zhou, S., Xu, J., Yang, Q.-H., *et al.*, 2013. Experiments and modeling of thermal conductivity of flake graphite/polymer composites affected by adding carbon-based nano-fillers. *Carbon* 57, 452–459.
- Zhou, T., Wang, X., Liu, X., Xiong, D., 2010. Improved thermal conductivity of epoxy composites using a hybrid multi-walled carbon nanotube/micro-SiC filler. *Carbon* 48 (4), 1171–1176.

Further Reading

- Amico, S.C., Angrizani, C.C., Drummond, M.L., 2010. Influence of the Stacking Sequence on the Mechanical Properties of Glass/Sisal Hybrid Composites. *Journal of Reinforced Plastics and Composites* 29 (2), 179–189.
- Cardoso, S.M., Chalivendra, V.B., Shukla, A., Yang, S., 2012. Damage detection of rubber toughened nanocomposites in the fracture process zone using carbon nanotubes. *Engineering Fracture Mechanics* 96, 380–391.
- Chand, N., Nigrawal, A., 2008. Investigations on D.C. conductivity behaviour of milled carbon fibre reinforced epoxy graded composites. *Bulletin of Materials Science* 31, 665–668.
- Dai, H.J., 2002. Carbon nanotubes: synthesis, integration, and properties. *Accounts of Chemical Research* 35, 1035–1044.
- Endo, M., Muramatsu, H., Hayashi, T., *et al.*, 2005. Nanotechnology: 'Buckypaper' from coaxial nanotubes. *Nature* 433, 476–477.
- Hollaway, L.C., 2010. A review of the present and future utilisation of FRP composites in the civil infrastructure with reference to their important in-service properties. *Construction and Building Materials* 24, 2419–2445.
- Meier, U., 2012. Carbon fiber reinforced polymer cables: Why? Why not? What if? *Arabian Journal for Science and Engineering* 37, 399–411.
- Pillai, S.K., Ray, S.S., 2011. Epoxy-Based Carbon Nanotubes Reinforced Composites. *Intech*. pp. 32–792.
- Reis, P.N.B., Ferreira, J.A.M., Antunes, F.V., Costa, J.D.M. 2007. Flexural behaviour of hybrid laminated composites. *Composites Part A: Applied Science and Manufacturing* 38 (6), 1612–1620.
- Saito, R., Matsuo, R., Kimura, T., Dresselhaus, G., Dresselhaus, M.S., 2001. Anomalous potential barrier of double-wall carbon nanotube. *Chemical Physics Letters* 348, 187–193.
- Subagia, I.D.G.A., Kim, Y., Tijing, L.D., Kim, C.S., Shon, H.K., 2014. Effect of stacking sequence on the flexural properties of hybrid composites reinforced with carbon and basalt fibers. *Composites Part B: Engineering* 58, 251–258.
- Thomann, U.I., Sauter, M., Ermanni, P., 2004. A combined impregnation and heat transfer model for stamp forming of unconsolidated commingled yarn preforms. *Composites Science and Technology* 64 (10–11), 1637–1651.
- Wu, C., Feng, P., Bai, Y., Lu, Y., 2014. Epoxy enhanced by recycled milled carbon fibers in adhesively-bonded CFRP for structural strengthening. *Polymer* 6, 76–92.
- Yahaya, R., Sapuan, S.M., Jawaid, M., Leman, Z., Zainudin, E.S. 2015. Effect of layering sequence and chemical treatment on the mechanical properties of woven kenaf–aramid hybrid laminated composites. *Materials & Design* 67, 173–179.
- Zhu, J., Kim, J.D., Peng, H., *et al.*, 2003. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. *Nano Letters* 3, 1107–1113.

Effect of Particle Size and Content of Crumb Rubber on the Dynamic Properties of Passenger Tyre Tread Using Finite Element Method

Adnan A Alshukri, University Putra Malaysia, Serdang, Selangor, Malaysia and State Company for Rubber and Tyres Industry, Najaf, Iraq
Faieza A Aziz, Mohd S Salit, and Nuraini A Aziz, University Putra Malaysia, Serdang, Selangor, Malaysia
Mohammed Al-Maamori, University of Babylon-Iraq, Babylon, Iraq

© 2019 Elsevier Inc. All rights reserved.

This is a reproduction of Adnan A. Alshukri, Faieza A Aziz, Mohd S Salit, Nuraini A Aziz, Mohammed Al-Maamori, Effect of Particle Size and Content of Crumb Rubber on the Dynamic Properties of Passenger Tyre Tread Using Finite Element Method, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2019, doi:10.1016/B978-0-12-803581-8.11339-6.

Introduction

Radial tyre is a complex structure with highly performance, made up of various types of composite materials. Rubber represents the matrix of this composite structure, to play the major role in vehicle supporting against the road roughness, generating maneuvering forces, providing safety and controlling stability. Because of its nonlinear nature in terms of material and geometry, rubber required many properties to characterize its behaviour.

Many theoretical models have characterized the mechanical behaviour of rubber. These models were developed based on a statistical thermodynamics approach (Treloar, 1973, 1975; Rosen, 1982), which stated that the decrease in entropy arises the elastic force of the rubber. Many research works are mostly focused on developing this approach, which reveals numerous models to characterize the rubber by a quantity known as the elastic strain energy density (W).

A plentiful of constitutive models have been proposed to describe elastomer behaviour, but a few of them are only able to characterize the complete non-linearity response of the material. Clearly, the most important models are those which able to specify the complete behaviours with a minimum number of material parameters, which must be investigated experimentally.

Finite element method based on these models is the most powerful tool which is normally utilized to imitate the static and dynamic behaviour of the tyres in various rolling and cornering states. In the last two decades, researchers used the commercial software of finite element to simulate the tyre dynamic problems. Goldstein (1996) utilized the Abaqus codes to mimic the radial truck tyre in slow rolling subjected to three dynamic cases. The conditions were, straight free rolling, braking, and cornering. Another software, LS-DYNA3D, was used by Kao and Muthukrishnan (1997) to simulate the tyre dynamic response for simple tyre model coupled with rigid wheel model. They revealed that, the dynamic behaviour of the tyre can be predicted from the design data, geometry, layout, material properties of various components, fiber reinforcement of the tyre, etc. The constitutive model of Mooney was adopted to describe the elastic properties of the rubber, while the strain energy function derived for the fiber-reinforced rubber were used to calculate the carcass properties. The calculated rim reaction forces agreed well with the experimental results.

Koishi *et al.* (1998) simulated the tyre cornering problem using an explicit finite element code, PAM-SHOCK, for the passenger tyre of size 175SR14. The research demonstrated the feasibility of the proposed simulation. To assess the accuracy of the model, the experimental results from the tyre test system, MTS Flat-Trac, were compared with the predicted results. The calculated cornering forces agreed well with the experimental results.

Campanac *et al.* (2000) studied the vibrations theories of the rolling tyre. They had introduced the heterogeneity produced by the tread pattern on the tyre belt in studying the vibration of the tyres, and showed that the tyre vibrations could be described by linear equations with time periodic coefficients.

Shiraishi *et al.* (2000) simulate the dynamic behaviours of a rolling tyre by an explicit finite element method. The complicated construction of the tyre was modeled exactly. The authors investigated several tyre properties for various rolling conditions. The findings showed that, there was a good agreement between the calculated and experiment results.

Kabe and Koishi (2000) had conducted a simulation of tyre cornering using codes of implicit and explicit finite element analysis. Where implicit finite element analysis represent the steady-state cornering simulation, and explicit described transient cornering simulation. The technique of moving reference frame for the case of implicit simulation required fine meshing in the contact area only. While, the fine meshing was also required in the circumferential direction of the tyre for explicit analysis. The predicted results were compared with experimental results. Good correlations were obtained between the predicted and measured data.

In this work, finite element model of a passenger tyre using Abaqus software was built to predict the dynamic performance of the tyre containing modified tread material. The material properties of the model are based on data extracted in the laboratory for the tread blend containing different particle size of waste tyre crumb rubber 40, 150, 180, 250, 425 and 600 μm at different weighted percentage 10%, 20%, and 30%. The crumb rubber of waste tyre is working as a virgin rubber replacement material. The proposed code should be able to analyze the tread performance when it becomes part of a real tyre structure.

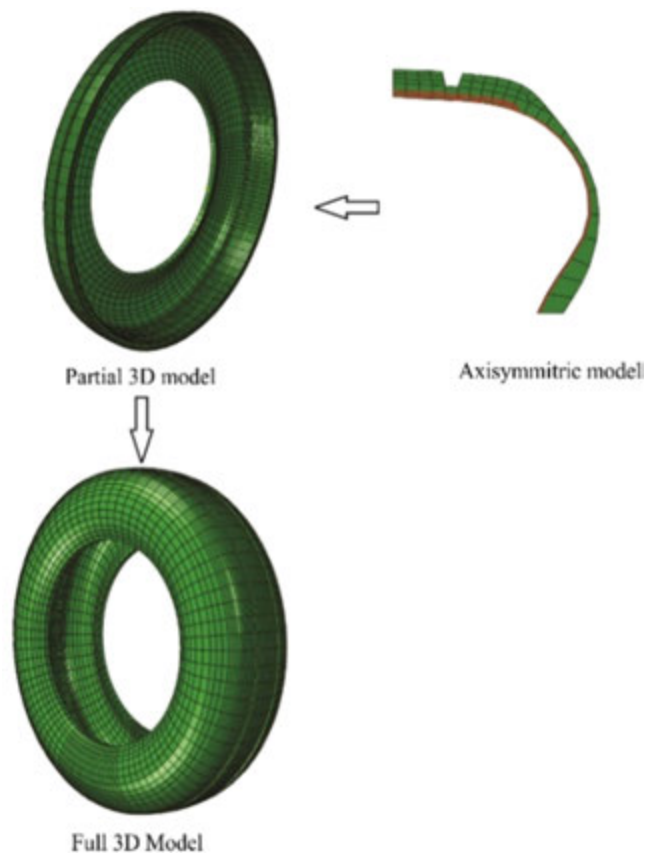


Fig. 1 Result transfer analysis sequence.

Modelling Method

The tyre was modeled in Abaqus using the technique of symmetric result transfer. This technique provides the ability to transfer results obtained from two-dimensional axisymmetric model or a partial three-dimensional model to full three-dimensional model. The capability of results transfer can considerably simplify and reduce the time and cost of the analyses of complex structures. According to this procedure, tyre simulation can be broken down into three separate analysis, axisymmetric two-dimensional model, partial three-dimensional model and full three-dimension model as shown in [Fig. 1](#).

The first simulation exploit the symmetry of the tyre model to use half cross section area of the tyre. This part of simulation was used to investigate the effects of inflation on the strain and stress component of the tyre elements. A complete two-dimensional result was extracted at the end of this step, and transferred to the second part of the simulation. This part is referred as a two-dimensional axisymmetric model.

The two-dimensional axisymmetric of the tyre cross section was revolved about the axis of revolution to produce the partial three-dimensional model, which is the second model of simulation. This part of simulation entails computation of static deformation shape of the inflated tyre under the vehicle dead load.

In the last part of the analysis, the result from the partial three-dimensional analysis was transferred to the full three-dimensional model. A complete tyre was produced by combining the two part of the partial three-dimensional model; one is the original part from the previous analysis and the second from the reflection of the partial three-dimensional model about the tier centerline. The effect of tread material modification on the tyre rolling performance was investigated during this analysis. The model is referred to as a full three-dimensional model. [Fig. 2](#). shows complete steps layout of three-dimensional analysis of rubber tyre utilizing the result transfer capability in Abaqus finite element software.

Tyre Material Simulation

The reinforcing materials used in the radial tyre structure were simulated as linear elastic materials and the required information was density, modulus of elasticity and poison ration for the steel cord belts and carcass, while the tread was modeled as hyperelastic materials with test data extracted from the mechanical test for each tread blend. The geometrical specifications such as direction, cross section area of the steel cord and spacing between each cord are also important to specify. The bead component was treated as a rigid body material. Material properties and dimensions used in this work are listed in [Table 1](#).

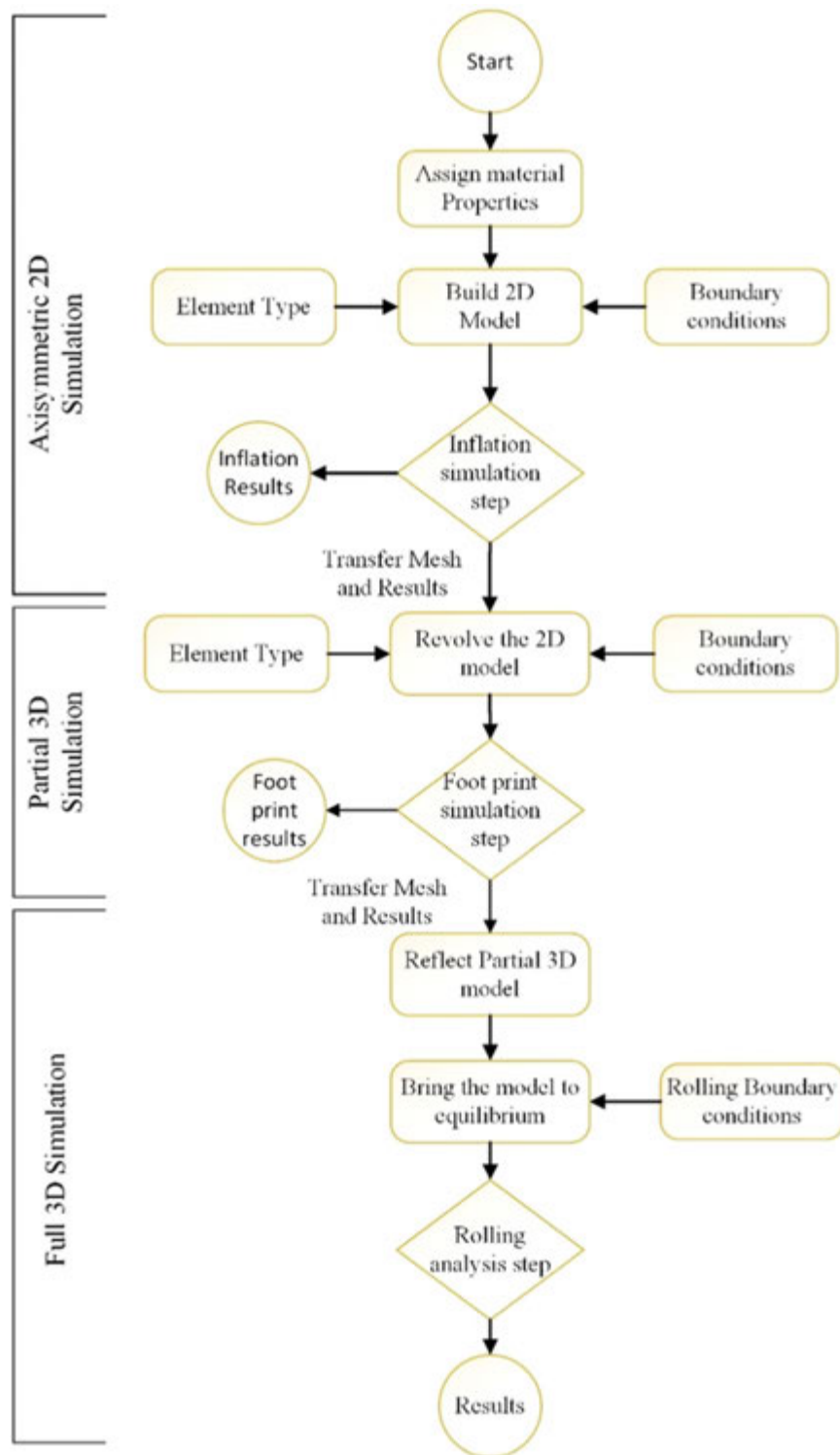


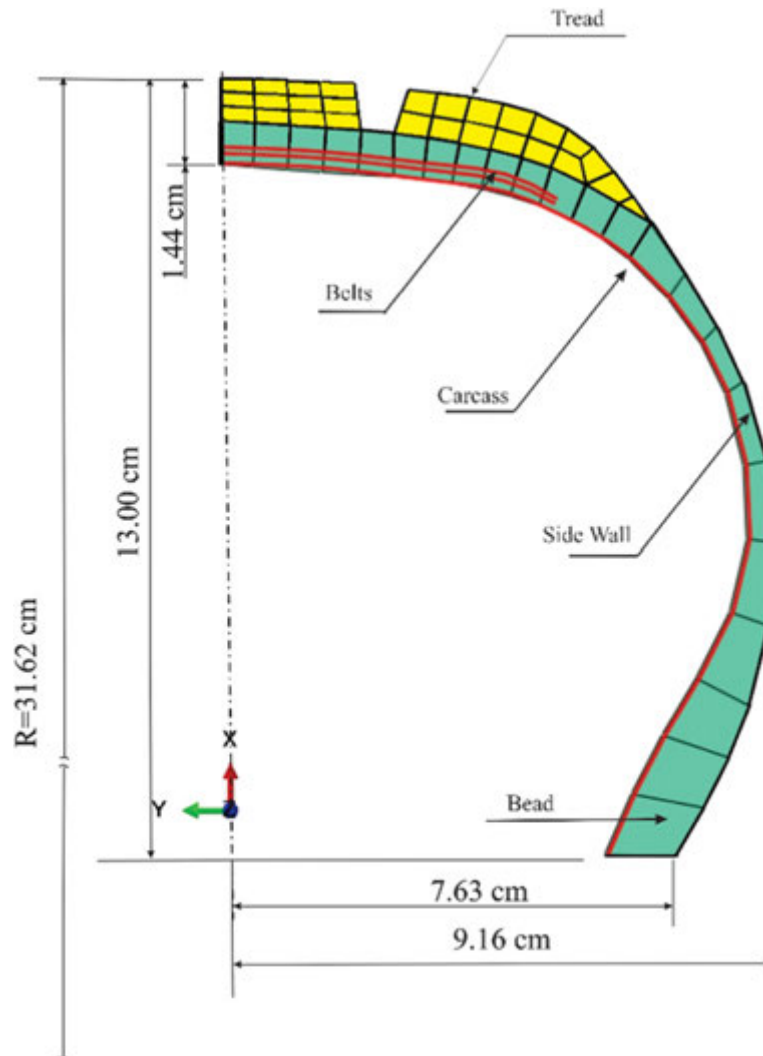
Fig. 2 Layout of complete steps of tyre analysis using Abaqus finite element software.

Steps of Simulation

The first step of simulation analysis uses the symmetry of the tyre geometry and utilizes the result transfer capability to simulate the effect of uniform internal pressure. The tread and sidewall components are made of rubber and the carcass and belts are made of rubber composite reinforced by textile fiber and steel cord respectively. The rubber is modeled as incompressible hyperelastic

Table 1 Reinforcing material specification

Component	Density ρ (Kg/m ³)	Modulus of elasticity E (N/m ²)	Poisson ratio ν	Area per bar (m) ²	Spacing (m)	Angle
Carcass textile	1500	9.87E9	0.3	4.208E-7	0.001	0
Belt1&2 steel cord	5900	202E9	0.3	2.118E-7	0.00116	110&70°

**Fig. 3** Axisymmetric model mesh.

material. For the entire section, elements type of continuum, generalized and axisymmetric type with four and three nodes hybrid (CGAX4H, CGAX3H) was used. While, the belts and carcass were modeled as surface elements of type (SFMGAX1) **Fig. 3**.

The second step of simulation is the foot-print solution of the tyre named as partial three-dimensional simulation. The code of "SYMMETRIC MODEL GENERATION" provided by Abaqus was used to generate a three-dimensional model from the set of element and nodes in the two-dimensional axisymmetric model as shown in **Fig. 4**. Element types of C3D6H and C3D8H were used corresponding to the two-dimensional element type. The boundary conditions applied to this part of simulation represent the displacement and the dead load that the tyre undergoes in the static condition. In this analysis, only half of the tyre was simulated; due to that reason, the load applied will be half of the total load carried by the tyre. For passenger tyre, the weight of the vehicle was divided into four, and half of this weight force will be used as the vertical load applied to the wheel center.

The last part of tyre analysis is three-dimensional model simulation, where the footprint results from the previous analysis is transferred to a full three-dimensional model. The two partial three-dimensional models (one part is the original part and the other part is the reflected one by "SYMMETRIC MODEL GENERATION" code) are combined together after reflecting the original mesh over the tyre center line **Fig. 5**.

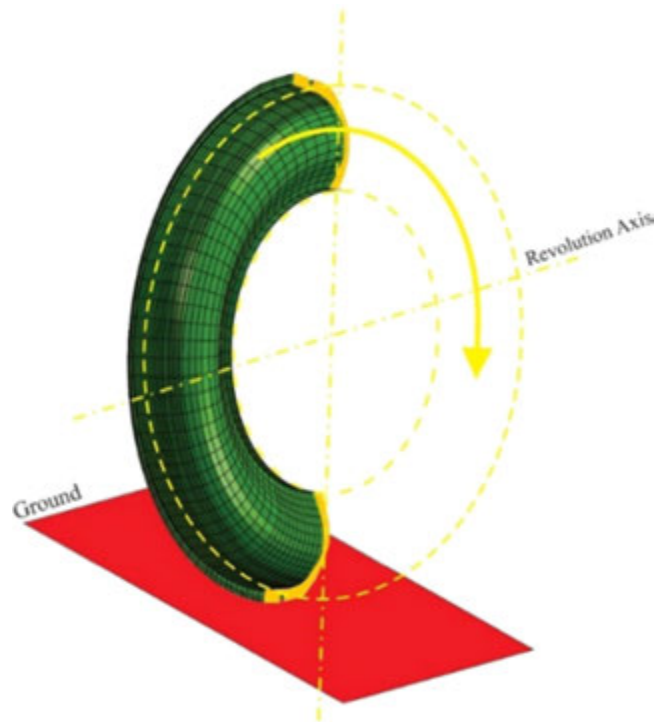


Fig. 4 The generation of partial three-dimensional model.

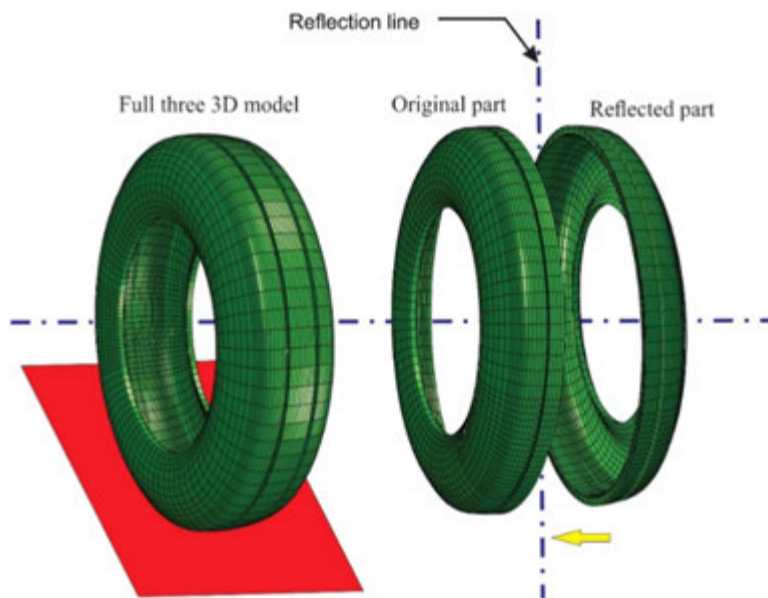


Fig. 5 Full three dimensional model.

The boundary conditions for the static solution of this step are inflation pressure (200 kPa) at the nodes of inside surface, and vehicle weight force (3300 N) applied to road reference node, while the dynamic boundary conditions are ground speed of 80 km and 3° slip angle.

The steady-state transport capability in Abaqus has been used in this model. This technique utilizes moving reference frame method in which Eulerian manner describes the rigid body rotation and Lagrangian manner describes the deformation region of the tyre. This kinematic description changes the contact problem of the steady state moving to pure spatially dependent simulation. Therefore, the mesh needs to be refined only in the contact region.

Mesh convergence was calculated based on maximum stress generated in the tyre during the rolling and cornering state with the total element number of (17425) as shown in Fig. 6.

A dynamic experimental data published by Kabe and Koishi (2000) was used in this study to verify the proposed finite element model. The collected data for radial tyre of passenger car's of size 235/45ZR17 was used. The tyre model was in contact with the road under a vertical load of 4 kN and traveling at 10 km/h (2.7778 m/s). The angular velocity of the tyre varied from 8 to 10 rad/s in order to determine the free rolling radius. The free rolling radius was estimated to be 313.28 mm. The cornering force generated at slip angle of 1° , 0° , and -1° were measured experimentally, and compared with the predicted values produced by the finite element model Fig. 7. Fig. 8 shows the cornering forces versus step time history at different slip angle produced by Abaqus

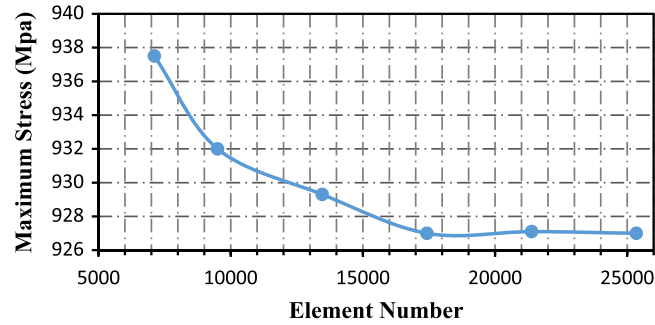


Fig. 6 Maximum stress convergence value.

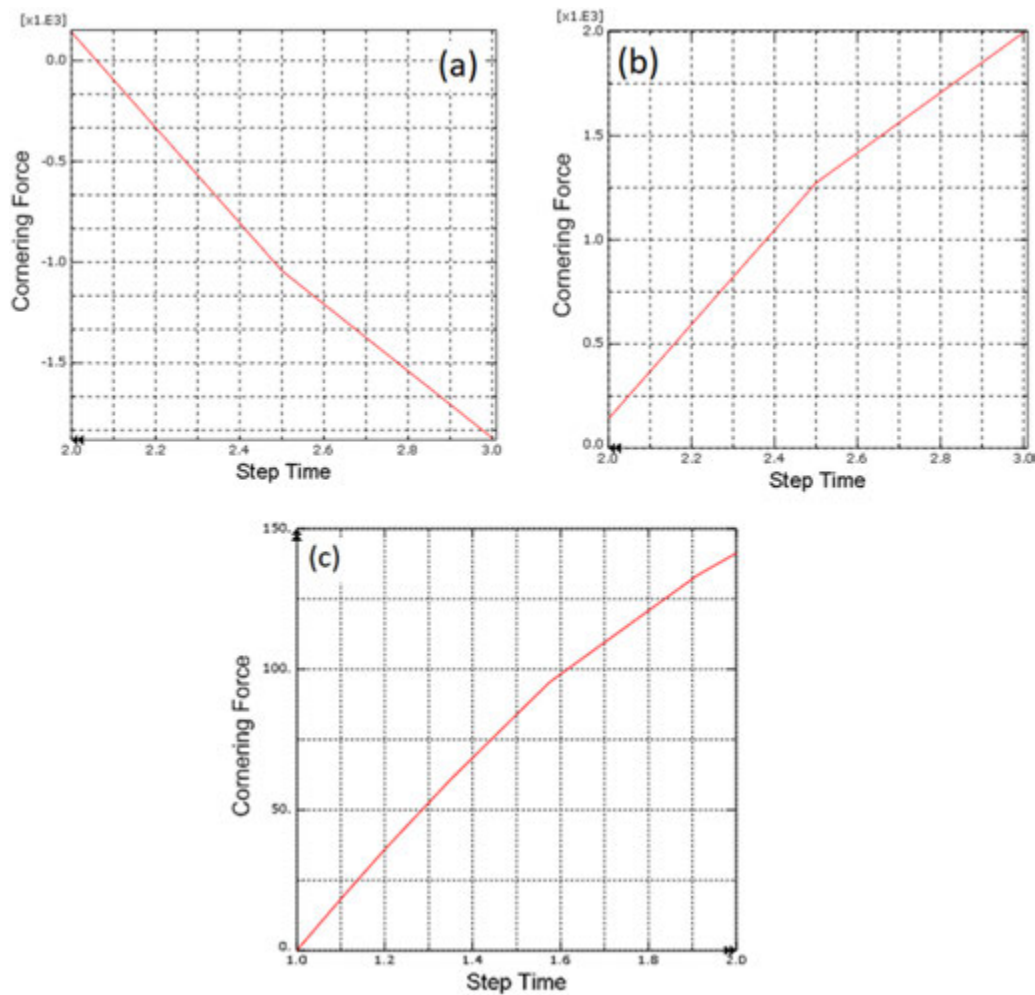


Fig. 7 Cornering force during analysis step time at (a) (-1°) slip angle, (b) (zero) slip angle, (c) (1°) slip angle produced by Abaqus.

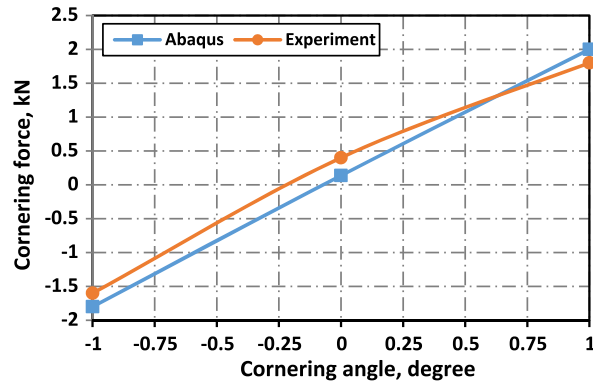


Fig. 8 Experimental and calculated cornering force at deferent slip angle.

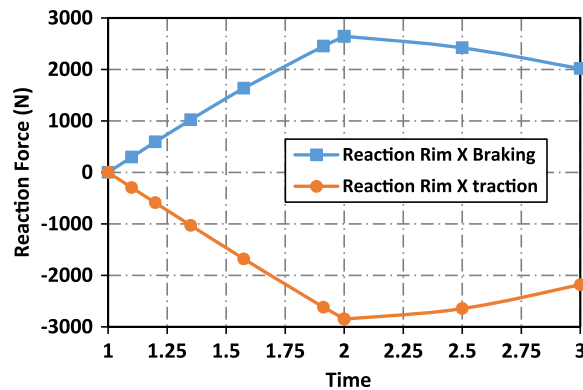


Fig. 9 Rolling force at rim in braking traction and slipping.

software. Fig. 9 shows a comparison between the experimental values and those calculated by Abaqus. The nonzero cornering force obtained at slip angle of 0° on both experiment and finite element is caused by play steer force due to the an isotropy of steel belt. The figure indicates that the calculated results by the Abaqus code agreed well with the experimental results.

Results and Discussion

In this research, the mechanical properties data of the material for different tread blends with different crumb rubber content and particle size, which were produced in the library, have been used to investigate the effect of tread layer properties on the tyre dynamic performance. The materials properties of each tread blend were introduced to the simulation model by test data option, which is available in Abaqus material section.

Hence, this model was used for all of the tyre tread blends under investigation. Tread blends with crumb rubber contents of 10%, 20% and 30% were investigated. Furthermore, the effect of crumb particle size of (40, 100, 180, 250, 425 and 600) μm was also studied. The material properties of other part of the tyre have been selected from the literature (Systèmes, 2012; Koishi *et al.*, 1998).

The rolling force, which is the reaction in the moving direction in braking and traction analyses, are shown in Fig. 10. The time of first step (1–2 s), represent the rolling reaction at 80 km/h, while the time of second step (2–3 s) represent the 3° cornering effect.

The effect of CR content and particle size on the axial force for the braking conditions is illustrated in Fig. 11. The figures show same behaviours for rolling resistance occurred in axial reaction forces. These behaviours can be explained by the raising of the modulus of elasticity with the reduction in CR content and particle size, which was determined from mechanical property test of the tread blend.

The strain energy for the whole system during the rolling and cornering condition for the braking and traction state is shown in Fig. 11. The value of strain energy in the static step was due to inflation and vehicle loading effect (step time from zero to one second). This value is reduced as the tyre starts rotating in the rolling step; this is due to the reduction in vertical load effect because of tyre inertia. The value of vertical force is a resultant of contact vertical reaction and vertical acceleration of the tyre mass (Captain *et al.*, 1979). As such, the force balance at the tyre axle in the vertical direction can be written as:

$$F_z = F_v - m\ddot{z} \quad (1)$$

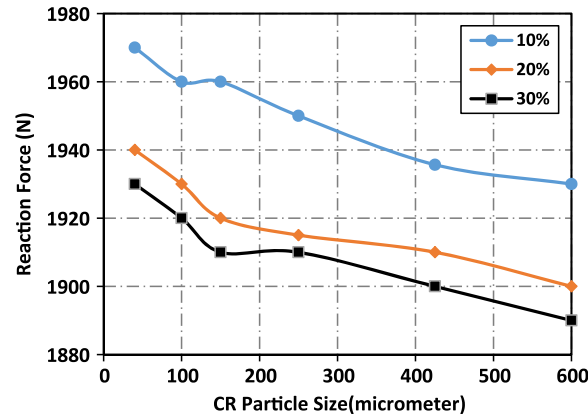


Fig. 10 Effect of loading and particle size of CR on the axial reaction at tyre rim at breaking.

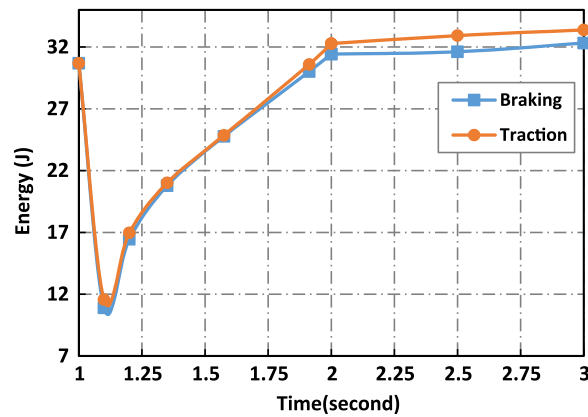


Fig. 11 Strain Energy density for the whole tyre model in the steps of rolling and cornering.

Where F_z is a vertical force at the tyre axle, F_v is a contact vertical reaction at tyre footprint; m is the mass of the tyre.

The value of strain energy increased as the tyre started rolling either in braking or traction state to reach its maximum value at the end of cornering step. While rolling, circumferential and lateral bending occurred due to the effect of the contact region. Thus, a frequent compression and stretching of all of the tyres layers accrued. The circumferential stress and strain during the rolling step are considered as a major contributor to inter laminar shear stress and strain, which leads to produce a propagated strain energy density within the rolling step (Chang *et al.*, 2003). The cornering state increases the strain energy slightly due to the addition of lateral force effect (Koishi *et al.*, 1998).

Figs. 12 and 13 present the effects of particle size and content of CR incorporated in the tread layer on the whole tyre strain energy at traction and braking state. The figures show that as the content and particle size of CR reduced the strain energy increased, and the content of 10% CR produce a higher rate of increase in comparison to the rate between 20% and 30%.

The force per unit area applied on the tyre surface in the contact patch can be decomposed into normal to ground component and tangential to the component. The normal component is a contact pressure. The contact pressure between tyre and road plays an important role in the design of tyres and roads through its major effects on the shear and normal stress in the contact patch to provide the desired driving or braking force (Marshak *et al.*, 1986). The distribution of contact pressure under rolling and cornering state for braking and traction conditions is shown in Fig. 14. The figure shows that for all cases, the maximum contact pressure is located in the shoulder zones with the rear region of the braking state Fig. 14(a), and front region with traction state Fig. 14(b). The cornering case shifts the maximum pressure toward the slipping direction to form a new force balance produced by the friction between tread and ground. These behaviours coincide with that stated by Narasimha Rao and Kumar (2007). The value of maximum pressure increased in the case of cornering due to the effect of contact area reduction through the slipping case; see Fig. 14(c) and (d).

Fig. 15 shows the comparison of the pressure distribution along the longitudinal contact patch, in the cases of braking and traction. The figure also shows that the peak pressure in the case of traction appeared in the front region to produce the required traction force, while in the case of braking, it appears at the rear region to create an opposite braking torque. The same behaviours was shown by Dorsch *et al.* (2002).

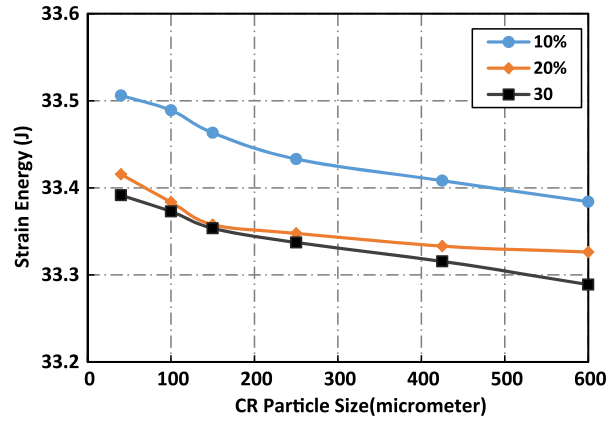


Fig. 12 Effect of CR particle size and content on the whole tyre strain energy at traction state.

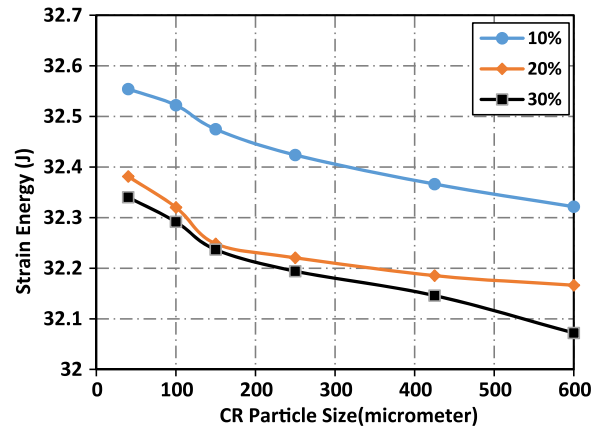


Fig. 13 Effect of CR particle size and content, on the whole tyre strain energy at braking state.

The effect of CR content used in tyre tread blend on the pressure distribution is shown in Fig. 16. The pressure increased with lower CR content in the tread blend due to the enhancement in the mechanical properties as the CR reduced, which produced better traction and braking stability. Same behaviour has been found for CR particle size as shown in Fig. 17.

The deformation behaviour of tyres in any direction x , y and z to the applied loads are important characteristic in tyre dynamics. This deformation depends mainly on the tyre stiffness in each direction and the value of applied load (Jazar, 2008).

$$F_x = k_x U_x \quad (2)$$

$$F_y = k_y U_y \quad (3)$$

$$F_z = k_z U_z \quad (4)$$

Where, F_x , F_y and F_z are the external forces on the tyre with k_x , k_y , k_z as tyre stiffness in each direction and U_x , U_y , U_z are the tyre strain in three directions.

In this work, the deformation has been measured at the contact patch where the maximum strain existed. The magnitude of strain vector has been taken into consideration to compare the effect of the different parameter on the tyre performance. Fig. 18 provides a contour plot for the deflection values which occur at the tyre during the rolling and cornering state of 80 km/h. As expected the maximum strain value is located at the contact patch which represents the elements that are subjected to maximum compression, tension and shear stress. As such, the deflection values for the elements along the contact patch were plotted in Fig. 19. The figure shows that there is a slight increase in the strain value when the content of CR in the tread layer increased. This is because of the reduction in CR content that produced higher stiffness of tread layer. Finally, the effect of braking and traction state has been illustrated in Figs. 20 and 21 respectively. From these figures, it is clear that the peak of strain is shifted towards the moving direction due to the position of maximum footprint pressure illustrated in Fig. 14. The cornering force applied to the moving tyre produced additional strain as shown in Fig. 21 where the value of strain increased from 23.3 mm for the rolling state to 28.3 mm for the cornering state.

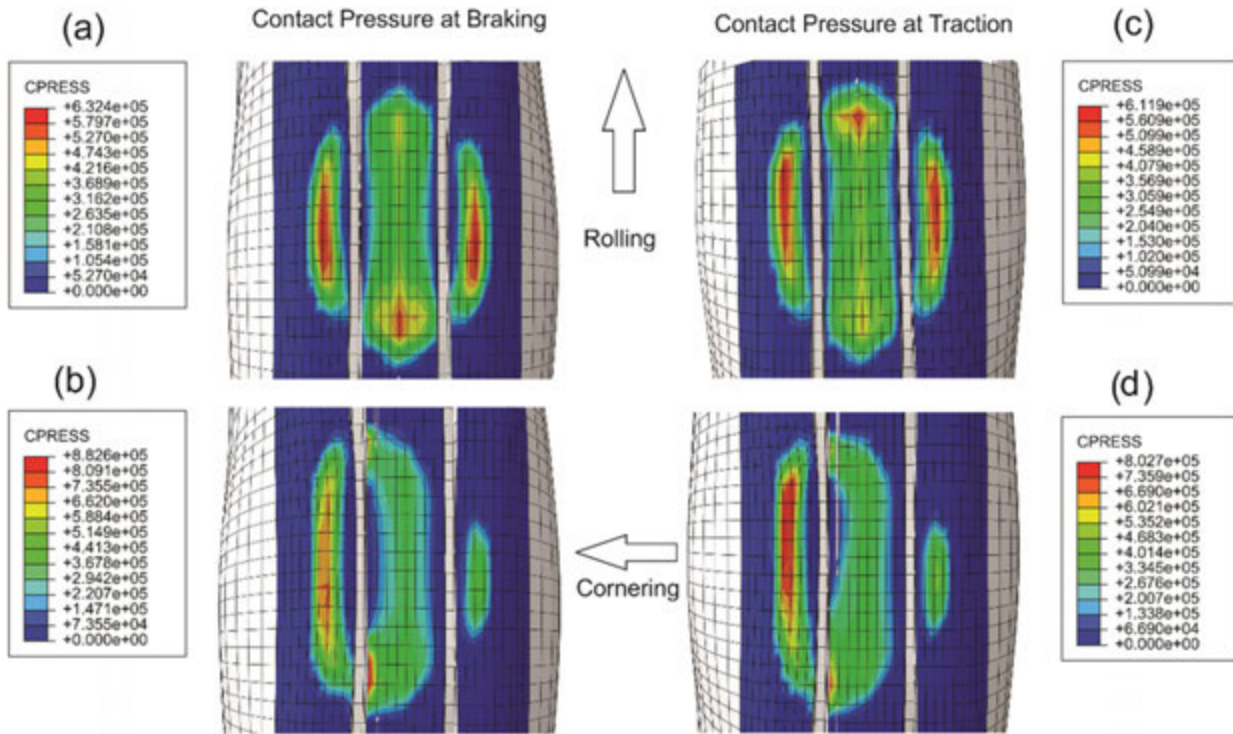


Fig. 14 Contact pressure distribution for tyre under (a) braking rolling, (b) braking and cornering, (c) traction rolling and (d) traction cornering conditions.

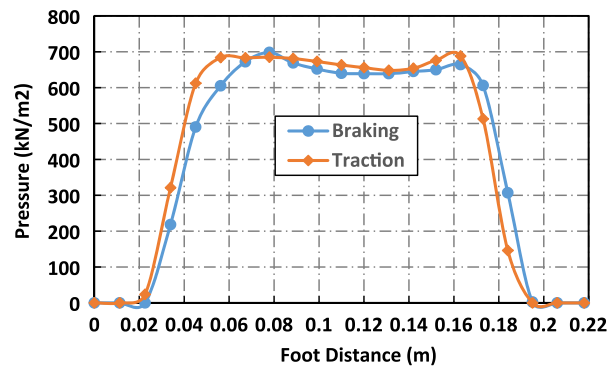


Fig. 15 Pressure along the contact patch at braking and traction cases.

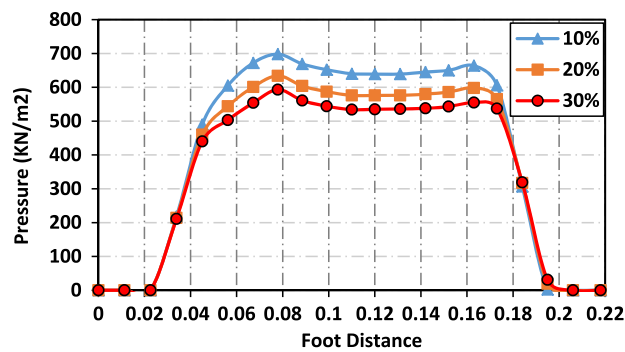


Fig. 16 Effect of CR content in tyre tread on the pressure distribution along the contact patch at braking case.

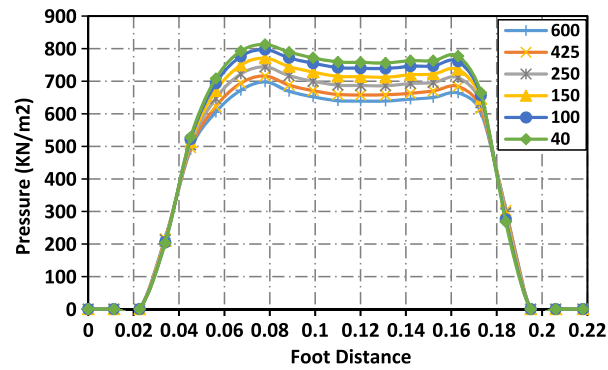


Fig. 17 Effect of CR particle size on the pressure distribution along the contact patch at braking case.

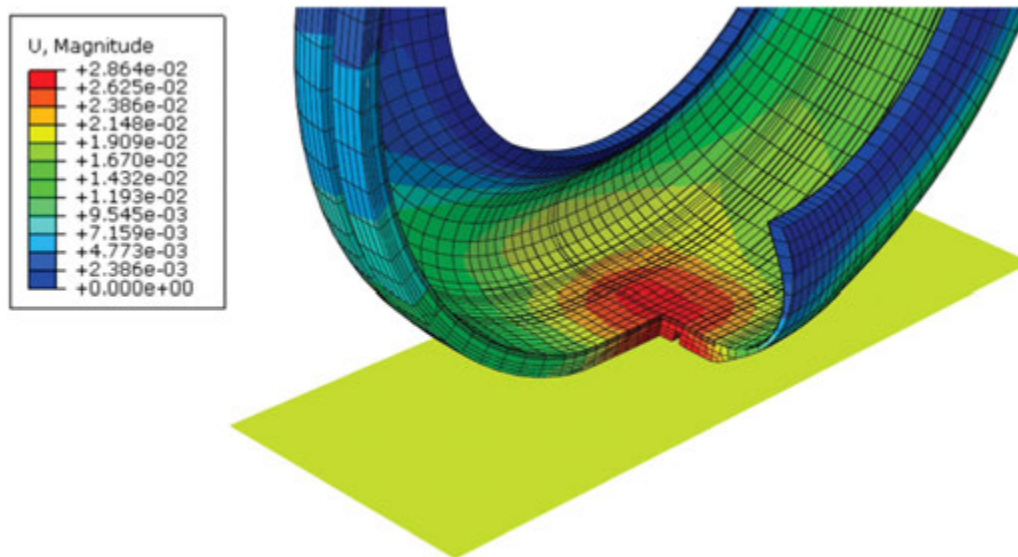


Fig. 18 Strain contour map for the tyre at rolling condition 80 km/h.

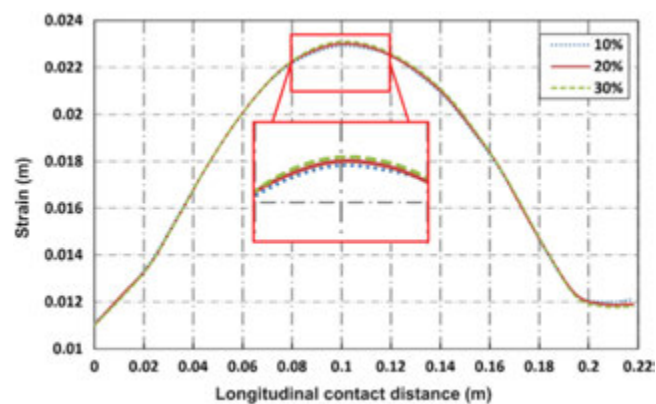


Fig. 19 Strain value for the elements along the contact patch for the state of rolling at different CR content.

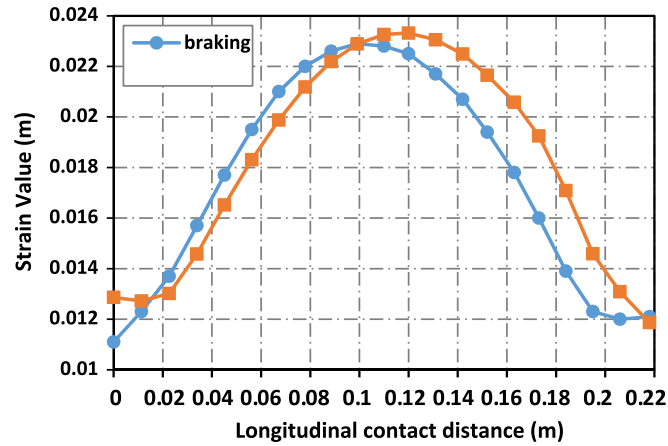


Fig. 20 Strain value for the elements along the contact patch for the state of rolling at braking and traction.

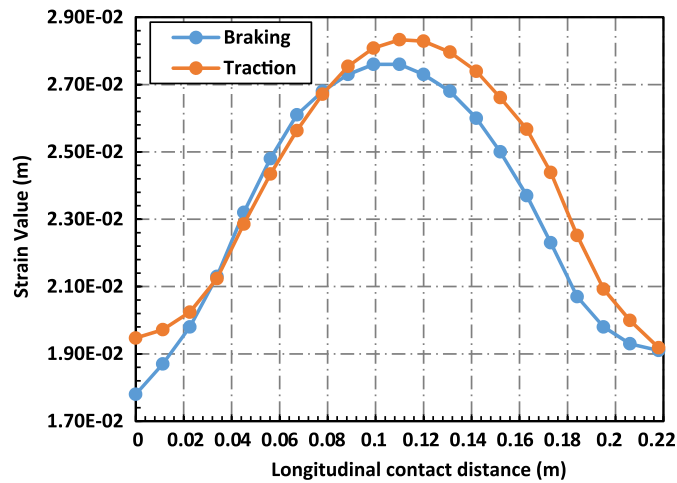


Fig. 21 Strain value for the elements along the contact patch for the state of rolling and cornering at braking and traction.

Conclusion

Many theoretical models from previous researches have characterized the mechanical behaviours of rubber. These models were utilized by finite element software to evaluate and simulate the hyper elastic material behaviours. A complete analysis based on Abaqus codes was performed for passenger tyre with special concern on the tyre tread behaviours. The experimental mechanical data for the tread blends at different CR particles size and contents were used to investigate the static and dynamic effects of using different CR in the tyre tread. The finite element code has proved efficient in simulating the effects of CR incorporation in tread blend. The code is capable of investigating the effects of material and shape design of any part of the tyre structure. The outcomes from the FEA model showed that the finer particle size of crumb rubber might increase the rolling resistance up to 2.5% as compared to a particle with coarse size. The low content of CR showed higher rolling resistance in braking and traction case. The analysis shows that the maximum strain energy was accrued at the finer CR size and lower contents. The model also helped in showing the maximum contact pressure regions in the cases of braking, traction and cornering.

Acknowledgement

This research was supported by State Company for Rubber and Tyres Industry/Iraq. We thank our colleagues from the laboratory of the company who provided insight and expertise that greatly assisted the research.

References

- Campanac, P., Nonami, K., Duhamel, D., 2000. Application of the vibration analysis of linear systems with time-periodic coefficients to the dynamics of a rolling tyre. *Journal of Sound and Vibration* 231 (1), 37–77.
- Captain, K., Boghani, A., Wormley, D., 1979. Analytical tire models for dynamic vehicle simulation. *Vehicle System Dynamics* 8 (1), 1–32.
- Chang, Y.-P., El-Gindy, M., Streit, D., 2003. Influence of tyre loading and inflation pressure on standing waves phenomenon using PAM-SHOCK. *International Journal of Heavy Vehicle Systems* 10 (1–2), 86–111.
- Dorsch, V., Becker, A., Vossen, L., 2002. Enhanced rubber friction model for finite element simulations of rolling tyres. *Plastics, Rubber and Composites* 31 (10), 458–464.
- Goldstein, A., 1996. Finite element analysis of a quasi-static rolling tire model for determination of truck tire forces and moments. *Tire Science and Technology* 24 (4), 278–293.
- Jazar, R.N., 2008. *Vehicle Dynamics. Theory and Applications*. Riverdale, NY: Springer Science + Business Media.
- Kabe, K., Koishi, M., 2000. Tire cornering simulation using finite element analysis. *Journal of Applied Polymer Science* 78 (8), 1566–1572.
- Kao, B., Muthukrishnan, M., 1997. Tire transient analysis with an explicit finite element program. *Tire Science and Technology* 25 (4), 230–244.
- Koishi, M., Kabe, K., Shiratori, M., 1998. Tire cornering simulation using an explicit finite element analysis code. *Tire Science and Technology* 26 (2), 109–119.
- Marshek, K.M., Chen, H.H., Connell, R.B., Hudson, R., 1986. Experimental determination of pressure distribution of truck tire-pavement contact. *Transportation Research Record* 1070, 9–13.
- Narasimha Rao, K., Kumar, R.K., 2007. Simulation of tire dynamic behavior using various finite element techniques. *International Journal for Computational Methods in Engineering Science and Mechanics* 8 (5), 363–372.
- Rosen, S.L., 1982. *Fundamental Principles of Polymeric Materials*. Wiley.
- Shiraishi, M., Yoshinaga, H., Miyori, A., Takahashi, E., 2000. Simulation of dynamically rolling tire. *Tire Science and Technology* 28 (4), 264–276.
- Systèmes, D., 2012. *Abaqus documentation*. Providence, RI, United States.
- Treloar, L., 1973. The elasticity and related properties of rubbers. *Reports on Progress in Physics* 36 (7), 755.
- Treloar, L.R.G., 1975. *The Physics of Rubber Elasticity*. USA: Oxford University Press.

Overview of Surface Roughness Effect on Silver Nanoparticle Filled Epoxy Composites

MA Salim, R Hamidi, and AM Saad, Technical University of Malaysia Melaka, Durian Tunggal, Melaka, Malaysia

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Mohd A. Salim, Roshidah Hamidi, Adzni Md. Saad, Overview of Surface Roughness Effect on Silver Nanoparticle Filled Epoxy Composites, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2019, doi:10.1016/B978-0-12-803581-8.11358-X.

Introduction

For conductive ink, there are two types of liquid with different viscosity and functionality that serve to carry the nanoparticles, namely the binder and the hardener. Epoxy is used as binder in this study and it is compatible with the viscosity behaviours of the ink. It shows the anticorrosion properties when acting as coating ingredients. While for the hardener, it is an additional substance to the ink mixture to produce strong or more durable ink finish and as well as the curing agent for epoxy. The final result of mixing these three components is a conductive ink that maintains its liquid form until it is printed on a surface at its drying point and able to conduct electricity.

In this study, troubleshooting problems in the characterization of conductive ink are elucidated in order to fabricate conductive ink which has high conductivity tracks or patterns. The characterization of conductive consists of the involved parameters, the formulation of ink loading, the printing procedure, ink-substrate interaction, the temperature to cure and post-treatment of ink.

For the formulation of ink loading, the interaction between filler, binder and hardener is important as it is the preliminary step to find out which ink loading can produce high conductivity. The ink loading is printed on the glass substrate, and then they will go through preheating method where the ink loading is cured in the oven for specific time and temperature. The characterization of conductive ink is investigated so that a proper understanding may be gained through various methods (analysis); four-point probe for sheet resistivity, contact profilometer for surface texture and light microscope for morphological analysis.

All these described steps are repeated for the ink loading in accordance to the composition of element to produce conductive ink. This study highlights two research questions about the formulation of silver nanoparticles-filled epoxy to produce conductive ink and the relationship between all of the investigated parameters for silver nanoparticles-filled epoxy.

The method of fabricating electrical circuits with the use of conductive ink will take place by using current method of creating circuit boards. The conductive ink depends on the formation of metal nanoparticles. Thus, the issues that need attention are the materials composition and its behaviour to have high conductivity ink as the drawback to conductive ink circuits is their resistance.

Crucial success factor for quick, simple and affordable production of PE prototypes and electronically functional prints is by choosing the accurate ink loading. One of the issues where the ink loading needs alteration is when the conductive ink is not fully dried after curing at certain temperature. Another issue is the ink-substrate interaction; the ink can easily come off of the substrate after printing or curing process, which indicates that a compatibility issue may come in between the ink and substrate, or the ink may not be dried adequately.

Recently, most researchers around the world studied the effect of conductive ink for silver nanoparticles-filled epoxy by implementing measurement techniques to conductive ink in order to maximize the quality and reliability of conductive ink through three techniques (Samano, 2017). These described techniques are sheet resistivity, surface texture and morphological behaviour for sheet resistivity. Samano described that four-point probe can measure the sample by producing no error with test lead resistance. Next, for the surface texture measurement, roughness is found as one of the main contributors that affect the electrical resistivity of printings on the substrate (Maattanen *et al.*, 2010) and imaging method from conventional microscope can contribute image with fine details that includes elemental details of printed sample (Ikeda *et al.*, 2007).

Based on these reports, all of the rising issues of the conductive ink are linked to the formulation of ink loading. It is also important to be mentioned about another additional factors such as material selection, printing method, curing temperature and others. Therefore, this study can potentially come out with the solutions for the stated problems.

This article discusses about the overview of surface roughness effect on silver nanoparticle filled epoxy composites for electronic packaging. Both directions, which are vertical and horizontal will be discussed in order to evaluate the surface roughness, and at the end of the study one conclusion is made.

Silver as Nanoparticle Materials

For the purpose of this article, only silver nanoparticles material is the subject being highlighted. Joshi (2011) and Burton (2008) described that silver maintains its reputation as the first option of end-users despite the fact that it is the most high-priced material in-use. It is due to the benefits of its high conductivity, even when oxidized as well as it can be simply formulated into inks and its adhesive properties toward substrate is better than nickel and copper.

Table 1 Metallic track comparison

	Sintering temperature	Thickness control	Ink stability (Clogging)	Solvent composition
Nanoparticle Inks	> 150°C	Deposition layers	Poor	Multiple
MOD Inks	70–130°C	Deposition layers	Good	Binary
Catalyst Inks	25–100°C	Reaction times	Excellent	Single
Reaction Inkjet System	Room temperature	Reaction concentration	Excellent	Single

In terms of printing conditions, inks must have high amount of silver and require sintering temperature of 150°C (Mosicki *et al.*, 2005). Allen stated that the printed patterns of nanoparticles inks with high resistivity need a process of sintering at elevated temperatures (100–200°C at 30–60 min) to distinguish stabilizers and/or some electrically non-conductive organic components to improve conductivity (Allen *et al.*, 2008).

Previous researchers were tabulated the benefits and drawbacks of nanoparticle inks as compared to other inks are listed in the Table 1.

Conductive Ink Characterization

Merilampi explained that the purpose of the characterization of conductive silver ink is to find out the parameters that can be improved in order to accomplish the desired properties of the ink in accordance to the conditions decided by different applications in 2015.

Electrical Properties

Joshi (2011) explained that the material resistance, which against the electric current flow is influenced by the dimensions of materials (the shape, length and area of cross sectional) and material chemical composition. Joshi added that the resistivity with SI units of Ohm-meter is corresponding to the conductivity with SI units of Siemens/meter.

The resistivity of the samples traces can be described as Eq. (1),

$$\rho = \frac{RA}{L} \quad (1)$$

where ρ is the resistivity, A is the cross-sectional area of the ink, L is sample trace length from end to end and R is the resistance recorded from the multi-meter.

The measured values of resistance after each sample being dried were used for the next calculation for resistivity of the sheet by the Eq. (1),

$$R_{SH} = R \times \frac{W}{l} \quad (2)$$

where l is the length of line in mm, W is the width in mm, R is the resistance in Ohm (Ω) and R_{SH} is the resistivity of the sheet in Ohm/sq, Ω /sq.

According to Nash *et al.*, the resistance of patterns was determined by using a four-point probe; when the probes were positioned on each of the lines, the current between the outer pins was set to $I = 100$ mA, and the voltage V across the inner pins being recorded. The resistance per unit length (l) was obtained by:

$$\frac{R}{l} = \frac{V}{I} \quad (3)$$

where the resistance per unit length is multiplied by the cross-sectional A in order to obtain the resistivity (Nash *et al.*, 2015).

Conductivity Versus Temperature

In 2008, Perelaer claimed that the conductivity will increase with the formation of an on-going percolation network throughout the printed pattern and the presence of metallic connection between the particles. Maissel added that the presence of a thin (as of a few nano-metres) residual organic layer among the particles of silver is adequate to avoid the movement of electrons between the particles in 1970. A rise in the temperature can distinguish the adsorbed dispersant that is possible to remain on the particles' surface (Perelaer *et al.*, 2008).

To acquire the possibly lowest resistance of the printed patterns, Perelaer proposed that the process of sintering is needed to convert the initial tiny contact regions to thicker necks, and finally to a dense layer. It is proved by Kim and Moon (2005) that the higher temperature causes the neck size to grow by adding densification. Thus, while this process is carried out, the connections among the particles become wider, which lead to the increasing of conductivity.

Research Methodology and Materials

The surface roughness of the sample can be identified by using portable contact profilometer. The measurement was taken at the same spot as microscopy and electrical were used as shown in Fig. 1.

Each substrate has two samples of ink layers located side by side that was labelled as Position A and Position B. Furthermore, every position is divided into three regions; Region 1, Region 2 and Region 3. The measurement took place at each region, but in the case of measuring the surface roughness, the measurement was taken in two directions, which were vertical and horizontal direction. Fig. 2 illustrates the region and direction of surface roughness measurement, and Fig. 3 shows the sample point of the measurement.

For the measurement of surface roughness, the sensor was put on the surface and then uniformly moved along the surface by driving the mechanism inside the instrument. Through the sharp built-in probe, the sensor captures the roughness of the surface. The roughness generates probe displacement, which causes the change in inductive quantity of induction coils and produces analogue signal. It is in the part of the surface roughness at output end of phase-sensitive rectifier. The signal then enters the system of data collection and these collected data are processed with parameter calculation and digital filtering by the chip. After that, the results are being displayed on LCD screen. The sample probe is shown in Fig. 4.

Before measuring the surface roughness, suitable probe of the sensor must be chosen since there are two types of probe either for flat surface or curved surface. Then, the sensor must be installed into the connection sheath located at the bottom of the instrument before the measurement is carried out. The probe is the major part of the instrument and acquires careful handling during the installation and unloading. It cannot be touched so as to prevent disturbance to the measurement data.

After the installation, the instrument was switched on and the related surface of the part was made sure to be clear. The instrument was placed (Fig. 5) stably and correctly on the surface to be measured and its position including the height was adjusted so that the pin of the probe to be in contact with the surface. The sliding trail of the probe must be parallel to the direction of process line on the surface according to the required directions; vertical or horizontal.

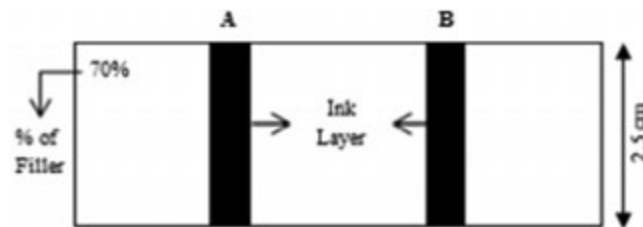


Fig. 1 Sketch of sample.

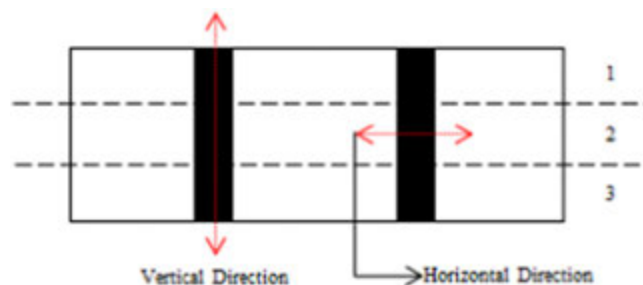


Fig. 2 Region and direction of measurement.

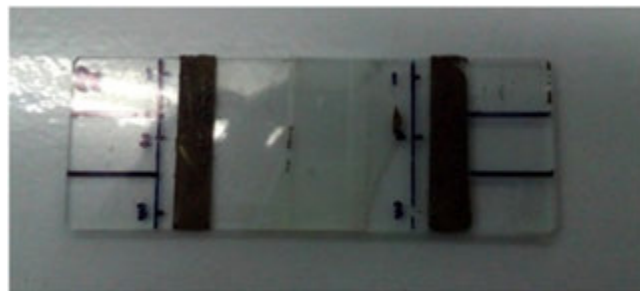


Fig. 3 Measured sample.



Fig. 4 Instruments and sensor.



Fig. 5 Positioning the instrument.

Then, the Start key was pressed to start the measuring process and the pin was let to finish the sliding. While the pin was sliding, the instrument and the sample must be held firmly to avoid them from moving around; otherwise the movement may cause the reading to be “out of range” displayed on the screen. After the sliding finished, the data was filtered and the instrument automatically stored the results; hence, displayed them on the screen.

Results and Discussion on Surface Roughness

In this study, Gökkaya and Nalbant explained that the parameter of surface to assess the surface roughness is the average of roughness, Ra that is also recognized as the centre line average (CLA) or arithmetic average (AA). The roughness average (Ra) is the integral of absolute value of profile roughness height over the length of evaluation, or the region between its centre line and profile of roughness (Gökkaya and Nalbant, 2007).

Surface Roughness in Vertical Direction

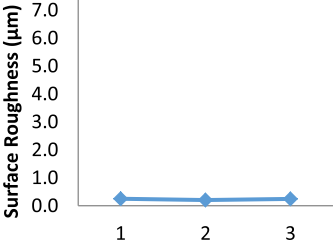
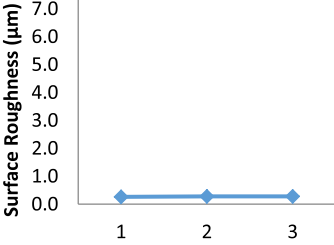
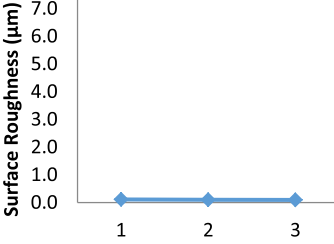
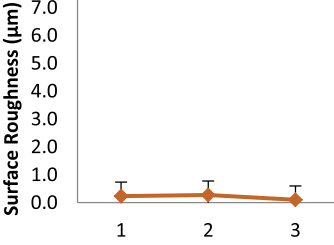
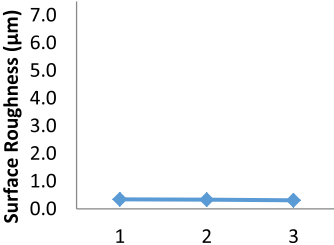
The results of the surface roughness for measurement in vertical and horizontal directions are shown in the table. All other parameters are remained constant so that only the surface roughness effect can be merely obtained. The vertical direction results are shown in [Table 2](#).

Each of the data is translated into the graph that represents three types of relation; relationship between surface roughness and number of measurement taken on the same spot, relationship between Ra and point of measurement and relationship between total Ra and measurement points at both positions. The details analysis of vertical results is shown in [Table 3](#) for 10% filler, [Table 4](#) for 20% filler, [Table 5](#) for 30%, [Table 6](#) for 40% filler, [Table 7](#) for 50% filler, [Table 8](#) for 60% filler, [Table 9](#) for 70% filler, [Table 10](#) for 80 % filler and [Table 11](#) for 90% filler, respectively.

Table 2 Vertical direction results

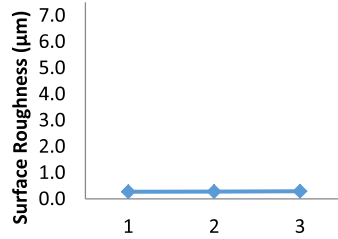
% of filler	Position	Surface roughness (μm)								
		Point 1	Average	Total average A & B	Point 2	Average	Total average A & B	Point 3	Average	Total average A & B
10	A	0.249	0.235	0.281	0.259	0.273	0.276	0.108	0.099	0.114
		0.208			0.279			0.099		
		0.247			0.280			0.091		
	B	0.344	0.328		0.271	0.279		0.124	0.129	
		0.330			0.277			0.112		
		0.310			0.290			0.150		
20	A	0.784	0.834	0.689	0.295	0.290	0.229	0.124	0.141	0.111
		0.880			0.292			0.178		
		0.839			0.284			0.121		
	B	0.537	0.544		0.190	0.168		0.090	0.081	
		0.548			0.164			0.081		
		0.546			0.150			0.071		
30	A	0.922	0.909	0.686	0.933	0.910	1.033	1.803	1.746	1.097
		0.916			0.915			1.696		
		0.889			0.883			1.738		
	B	0.482	0.463		1.171	1.156		0.483	0.447	
		0.459			1.128			0.435		
		0.448			1.169			0.424		
40	A	0.696	0.768	0.561	0.398	0.426	0.364	0.306	0.317	0.300
		0.807			0.411			0.323		
		0.801			0.469			0.321		
	B	0.320	0.354		0.311	0.302		0.293	0.282	
		0.370			0.291			0.257		
		0.371			0.303			0.297		
50	A	0.285	0.286	0.245	0.247	0.241	0.240	0.367	0.383	0.383
		0.285			0.240			0.385		
		0.288			0.237			0.396		
	B	0.205	0.204		0.239	0.239		0.367	0.383	
		0.203			0.240			0.385		
		0.203			0.237			0.396		
60	A	3.409	3.509	4.264	2.709	2.726	4.006	2.300	2.349	2.319
		3.547			2.724			2.407		
		3.570			2.745			2.341		
	B	5.048	5.020		5.270	5.286		2.323	2.288	
		5.023			5.283			2.276		
		4.989			5.306			2.266		
70	A	3.977	3.753	4.434	5.014	4.981	3.736	2.890	2.850	3.257
		3.669			4.992			2.852		
		3.613			4.938			2.807		
	B	5.045	5.114		2.463	2.490		3.707	3.665	
		5.226			2.502			3.657		
		5.071			2.506			3.631		
80	A	5.266	5.378	4.299	3.509	3.397	3.461	2.271	2.254	2.169
		5.370			3.387			2.260		
		5.499			3.294			2.232		
	B	3.146	3.220		3.628	3.526		2.020	2.084	
		3.166			3.541			2.088		
		3.349			3.409			2.145		
90	A	5.220	5.199	5.721	5.192	5.477	5.890	4.700	4.490	5.716
		5.151			5.644			4.352		
		5.226			5.596			4.417		
	B	6.240	6.242		6.248	6.303		6.890	6.943	
		6.170			6.276			6.921		
		6.316			6.384			7.017		

Table 3 Analysis of vertical results for 10% of filler

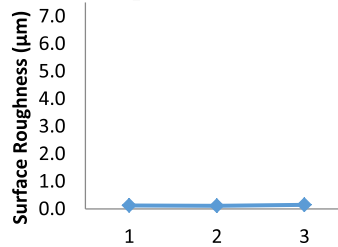
Vertical Results	Analysis
Sample A at Point 1  Position A It has low surface roughness that is in the range of 0.2–0.25 µm, which means that the result has stable consistency.	
Sample A at Point 2  The graph illustrates low surface roughness where the range is 0.25–0.3 µm, but it increases as compared to the previous point.	
Sample A at Point 3  This area has the lowest surface roughness that is in the range of 0–1 µm, which means that it has the smoothest surface.	
Average Sample A  At point 3, Ra between three points is the lowest as compared to the other two points, but the sample still has smooth surface. The error bar appears to be short since the difference between the highest and the lowest values at each point are 0.041 µm, 0.021 µm and 0.018 µm.	
Sample B at Point 1  Position B It has the highest surface roughness value as compared to other points in both positions, but in consistent range.	

Sample B at Point 2

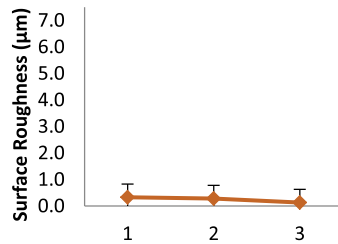
The graph illustrates low surface roughness with small gap of value between the times of data reading.

**Sample B at Point 3**

It has the lowest surface roughness value as compared to the value in this position. At third reading when the data is taken, the value slightly increases.

**Average Sample B**

At the first and second points the data is taken, Ra is consistent while at the third point, the value decreases, but the sample is still in homogenous solution since the value gap is small. The error bar appears to be short since the difference between the highest and the lowest values at each point are 0.034 µm, 0.019 µm and 0.038 µm.

**Total Average A & B***Total average at positions A & B*

At point 1 and 2, total Ra is consistent while at point 3, it decreases in value but in small gap, which describes that the sample is in homogenous solution. The error bar can barely be seen, which proves that the total average values are more certain.

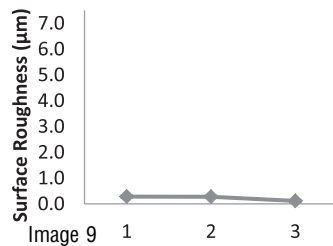
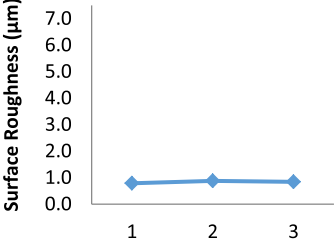
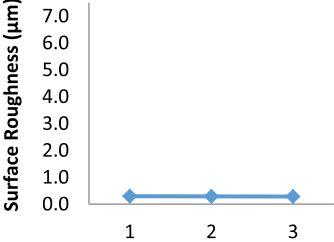
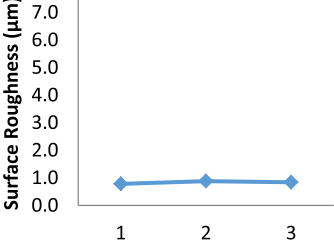
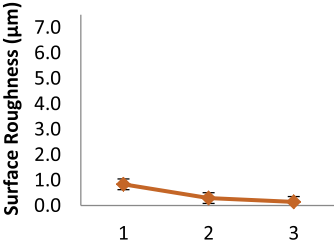
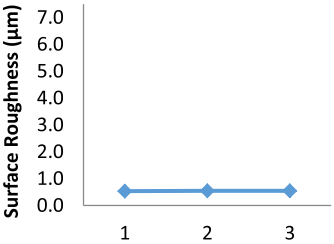
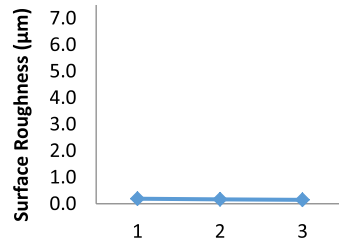
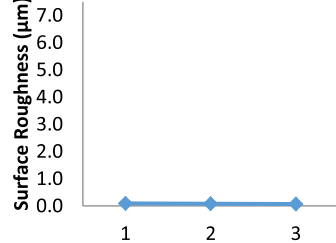


Table 4 Analysis of vertical results for 20% of filler

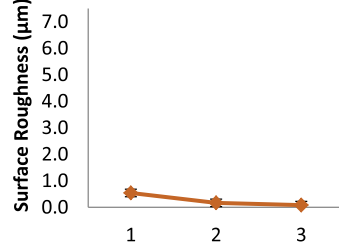
Vertical Results	Analysis
Sample A at Point 1 	<i>Position A</i> It has the highest value of surface roughness for 20% of filler, which is in the range of 0.7–0.9 µm.
Sample A at Point 2 	The value of surface roughness is consistent since the gap of value between the reading times of data taken is small.
Sample A at Point 3 	The graph illustrates the lowest surface roughness value at this position with the range of 0.12 µm until 0.18 µm.
Average Sample A 	There is decreasing of Ra from the first reading to the second and third readings with the difference in Ra value between the first and second reading is 0.46 µm. The error bar is in small dimension, which coming from the difference between the highest and the lowest values at each point with the values of 0.055 µm, 0.011 µm and 0.057 µm.
Sample B at Point 1 	<i>Position B</i> Graph illustrates that the value of surface roughness is the highest at this position where the data is 0.5 µm and above.

Sample B at Point 2

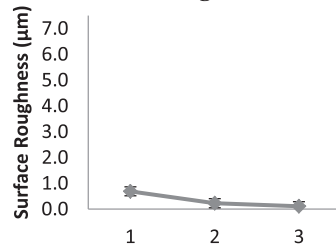
From the graph, the data from third reading shows slight decrement of surface roughness value.

Sample B at Point 3

Graph illustrates that it has the lowest value range of surface roughness, which is below 0.1 μm where the graph shows the consistency between the data.

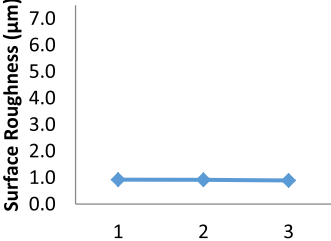
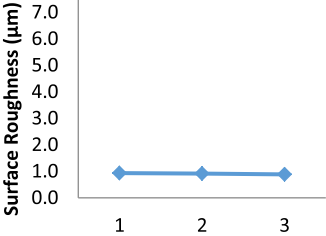
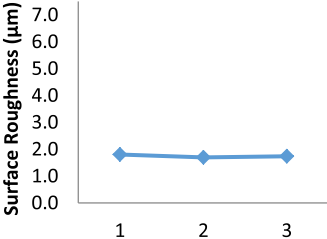
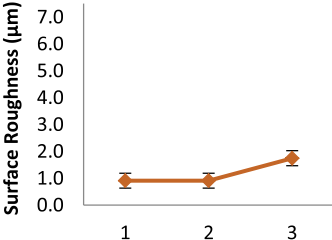
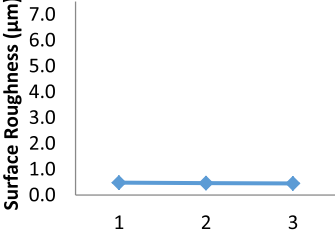
Average Sample B

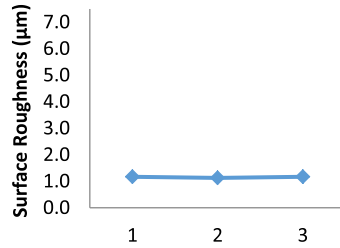
The same as at position A, Ra starts to decrease at point 1 from 0.689 to 0.229 μm; but between point 2 and point 3, there is small difference in their data. The error bar can barely be seen since the difference between the highest and the lowest values at each point are below 0.04 μm.

Total Average A & B*Total average at positions A & B*

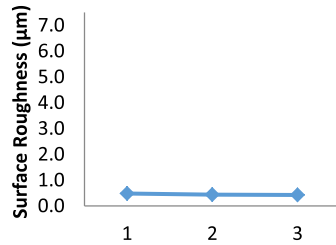
The graph displays similar condition with Average Sample A and Average Sample B where at the first point; total Ra starts to decrease but consistent at point 2 and point 3. The error bar can barely be seen, which proves that the total Ra values are more certain.

Table 5 Analysis of vertical results for 30% of filler

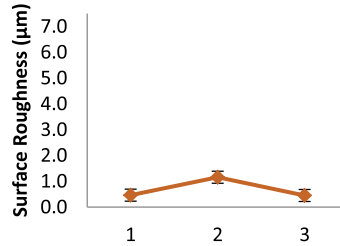
Vertical results	Analysis
Sample A at Point 1  Position A From the graph, the data can be seen to have the consistency since the difference of surface roughness value between reading time is small.	
Sample A at Point 2  The graph also shows consistency since the gap between the surface roughness values is small but there is slightly decreasing value at third reading.	
Sample A at Point 3  The data displays slight difference among all of the three readings since the range between the highest value and the smallest value is small.	
Average Sample A  Through the graph, Ra starts to increase from Reading 2 to Reading 3 with the difference value of 0.836 μm while the data keeps consistent between the first and second readings. The error bar is in small dimension, which coming from the difference between the highest and the lowest values at each point that is 0.107 μm and below.	
Sample B at Point 1  Position B The graph is consistent since there is no big difference between their values of surface roughness.	

Sample B at Point 2

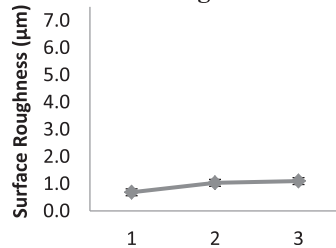
At first and third readings, the data is consistent, but for second reading, the data is a bit decreasing in value.

Sample B at Point 3

The graph also has the same condition as at point 1 where the difference between the values of surface roughness is small.

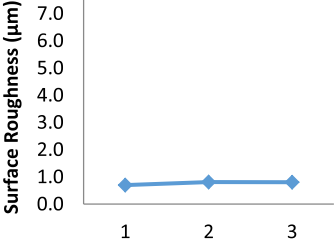
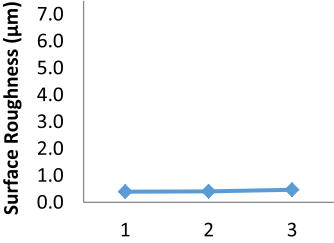
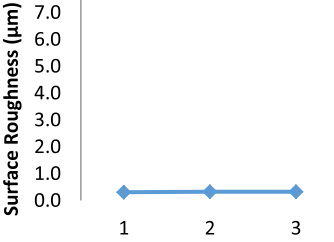
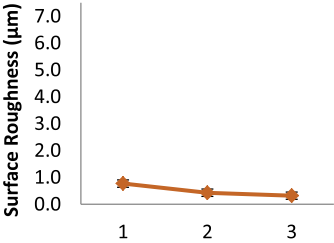
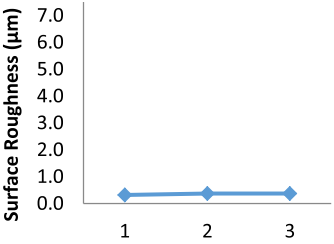
Average Sample B

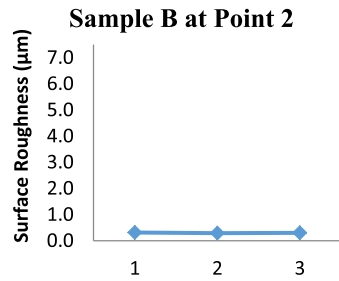
As can be seen in the graph, the Ra value from second reading has obvious difference as compared to the average value from first and second readings. The difference value between Reading 1 and Reading 2 is 0.693 µm while between Reading 2 and Reading 3, the difference value is 0.709 µm. Thus there is no consistency in their values. The error bar is in short dimension, which is caused by the highest value is 1.171 µm and the lowest value is 0.424 µm.

Total Average A & B**Total average at positions A & B**

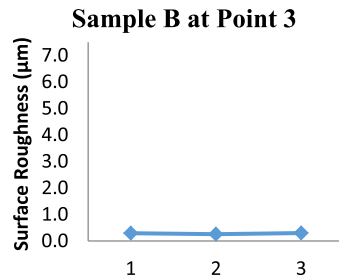
The total of Ra keeps increasing across the three points, but at point 2 and point 3; they have small gap in data. The error bar can barely be seen, which proves that there is small difference between the average values.

Table 6 Analysis of vertical results for 40% of filler

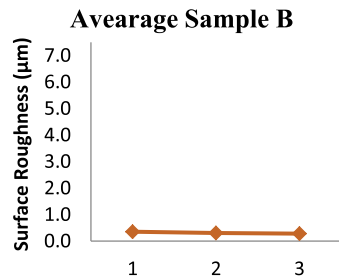
Vertical Results	Analysis
Sample A at Point 1  Sample A at Point 2  Sample A at Point 3  Average Sample A  Sample B at Point 1 	Position A The value of surface roughness at this point is the highest for 40% of filler, which ranges up to 0.8 μm. The graph shows small increment of value at Reading 3 as compared to two other remaining readings. The data displays up to no difference among all of the three readings since their values are around 0.3 μm. Ra value is the highest at point 1 but the average value starts to decrease at point 2 and point 3. The error bar can barely be seen since the difference between the highest and the lowest values at each point is not exceeding over 0.12 μm. Position B The value from the second and third readings shows consistency but differs from the value at Reading 1 that has lower value as compared to the other two values.



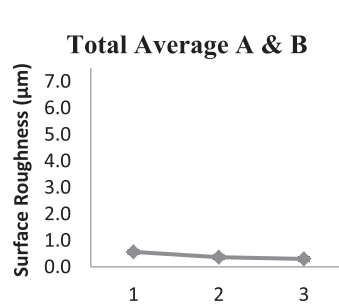
Graph displays consistency among all of the three readings lead by the small difference in their values of surface roughness.



The graph illustrates that it has the lowest value of surface roughness for this sample that is in the range of 0.2–0.3 µm.



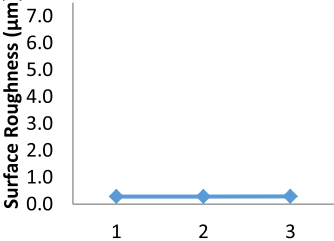
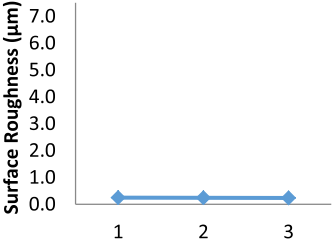
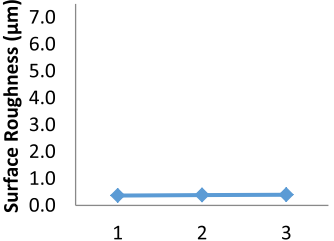
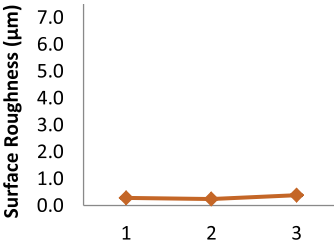
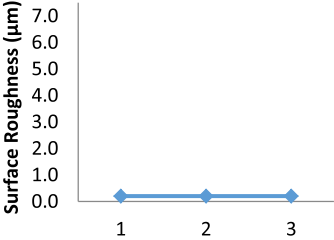
From the graph, the data shows consistency among the three readings, which proves that there is up to no difference in Ra values. The error bar can barely be seen, which proves that there is small difference between the average values.



Total average at positions A & B

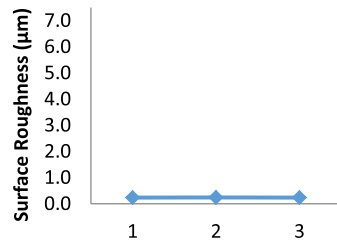
Total average values at point 2 and point 3 show consistency but they are lower as compared to the total value of Ra at the first point. The error bar can barely be seen, which explains that the total average values are more certain.

Table 7 Analysis of vertical results for 50% of filler

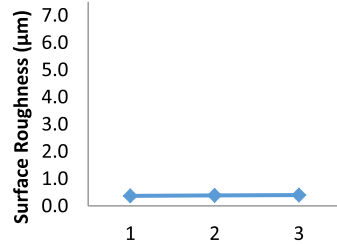
Vertical Results	Analysis
Sample A at Point 1  Position A The graph exhibits a stable consistency among the values since the difference in their value of surface roughness is up to no difference at all.	
Sample A at Point 2  The graph also experiences the similar situation as in the previous graphs where the data being displayed has small difference.	
Sample A at Point 3  The values from Reading 1 and Reading 2 are consistent but at Reading 3, the value is slightly increasing.	
Average Sample A  From Point 3, the increasing average value is obvious while the average values at Point 1 and Point 2 are consistent. The error bar can barely be seen which causes by the difference between the highest and the lowest values at each point is only up to 0.03 µm.	
Sample B at Point 1  Position B From this point, it has the lowest value of surface roughness for 50% of filler and exhibits the consistency in their values as can be seen in the graph.	

Sample B at Point 2

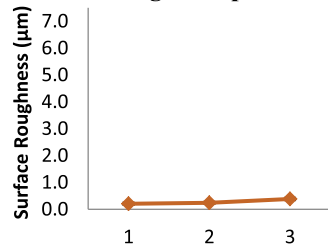
The graph also displays that the values of surface roughness at this point have stable consistency.

**Sample B at Point 3**

The graph illustrates that the values of surface roughness among all of three readings also have consistency.

**Average Sample B**

At Point 3, the average value is at its highest while the rests show small up to no difference in their average values. The error bar can barely be seen due to the difference between the highest and the lowest values at each point is only escalated up to 0.03 μm.

**Total Average A & B***Total average at positions A & B*

The total average values for all of three points have small difference but the total average at point 3 is a bit higher as compared to other points. The error bar can barely be seen, which describes that the total average values are more certain.

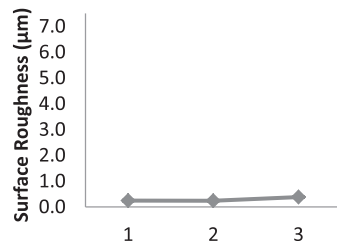
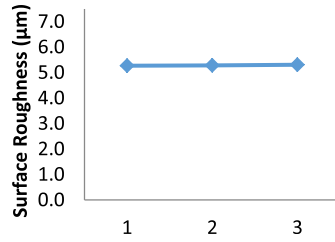
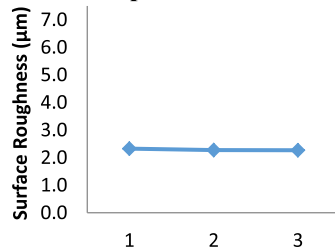


Table 8 Analysis of vertical results for 60% of filler

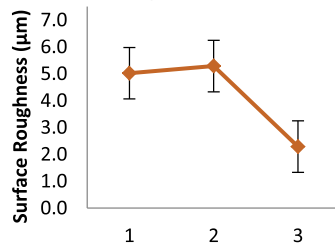
Vertical Results	Analysis								
Sample A at Point 1 <table><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>3.5</td></tr><tr><td>2</td><td>3.7</td></tr><tr><td>3</td><td>3.7</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	3.5	2	3.7	3	3.7	Position A The values rapidly increasing from the previous percentage of fillers where they start from 2 μm and above. From the graph, the values at Reading 2 and Reading 3 are consistent while at Reading 1, the value is a bit lower.
Reading	Surface Roughness (μm)								
1	3.5								
2	3.7								
3	3.7								
Sample A at Point 2 <table><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>2.7</td></tr><tr><td>2</td><td>2.7</td></tr><tr><td>3</td><td>2.7</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	2.7	2	2.7	3	2.7	The graph displays stable consistency since their range is consistent that is around 2.7 μm.
Reading	Surface Roughness (μm)								
1	2.7								
2	2.7								
3	2.7								
Sample A at Point 3 <table><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>2.3</td></tr><tr><td>2</td><td>2.5</td></tr><tr><td>3</td><td>2.4</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	2.3	2	2.5	3	2.4	The value from Reading 2 is a bit higher as compared to the values from Reading 1 and Reading 3 that are consistent between each other.
Reading	Surface Roughness (μm)								
1	2.3								
2	2.5								
3	2.4								
Average Sample A <table><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>3.5</td></tr><tr><td>2</td><td>2.7</td></tr><tr><td>3</td><td>2.3</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	3.5	2	2.7	3	2.3	There is no stable consistency among the average values being displayed in the graph as the difference value between the highest and the lowest data is 1.16 μm. The error bar is in short length due to the difference between the highest and the lowest values at each point are 0.138 μm, 0.036 μm and 0.107 μm.
Reading	Surface Roughness (μm)								
1	3.5								
2	2.7								
3	2.3								
Sample B at Point 1 <table><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>5.1</td></tr><tr><td>2</td><td>5.1</td></tr><tr><td>3</td><td>5.0</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	5.1	2	5.1	3	5.0	Position B The graph exhibits consistency in the data but the value from Reading 3 is slightly lower than the other values.
Reading	Surface Roughness (μm)								
1	5.1								
2	5.1								
3	5.0								

Sample B at Point 2

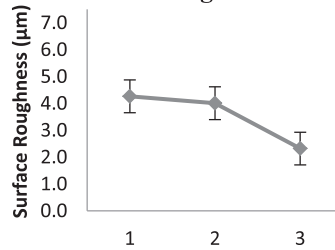
At this point, the value of surface roughness is the highest for this sample with the range of 5.2–5.3 μm .

Sample B at Point 3

It has the lowest value of surface roughness for 60% of filler that is in the range of 2.3–2.8 μm while the data shows consistency in their values.

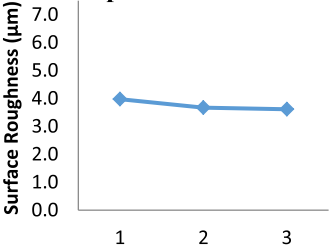
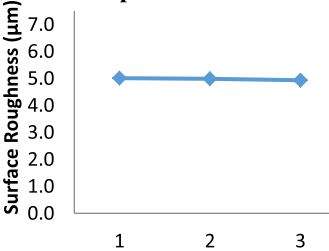
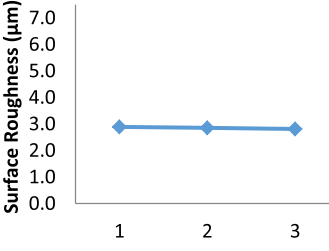
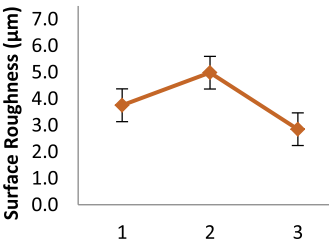
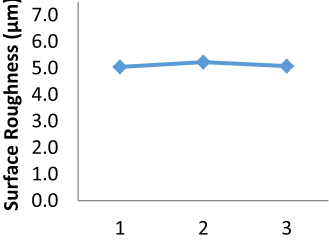
Average Sample B

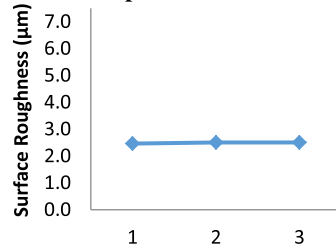
The average values at point 1 and point 2 have small difference but the value drops rapidly at point 3 as can be seen in the graph. The error bars show long dimension, which means that the concentration of calculated average values is low.

Total Average A & B*Total average at positions A & B*

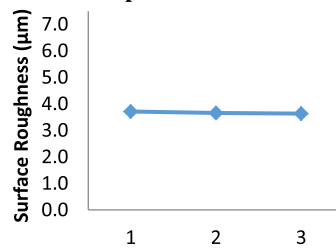
The total average value at point 3 has big gap as compared to the values at point 1 and point 2 as it experiences high decreasing of value. The error bar displays big difference, which means that the total average values of surface roughness are uncertain.

Table 9 Analysis of vertical results for 70% of filler

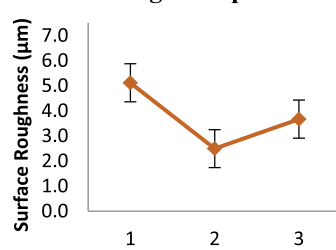
Vertical Results	Analysis								
Sample A at Point 1  <table border="1"><caption>Data for Sample A at Point 1</caption><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>4.0</td></tr><tr><td>2</td><td>3.7</td></tr><tr><td>3</td><td>3.6</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	4.0	2	3.7	3	3.6	<i>Position A</i> From Reading 1, the surface roughness value is the highest while the other values at Reading 2 and Reading 3 have small gap between each other, which leads to consistency.
Reading	Surface Roughness (μm)								
1	4.0								
2	3.7								
3	3.6								
Sample A at Point 2  <table border="1"><caption>Data for Sample A at Point 2</caption><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>5.0</td></tr><tr><td>2</td><td>5.0</td></tr><tr><td>3</td><td>5.0</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	5.0	2	5.0	3	5.0	The data produces a consistent graph plot since there is small gap between all of the surface roughness values.
Reading	Surface Roughness (μm)								
1	5.0								
2	5.0								
3	5.0								
Sample A at Point 3  <table border="1"><caption>Data for Sample A at Point 3</caption><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>2.8</td></tr><tr><td>2</td><td>2.8</td></tr><tr><td>3</td><td>2.8</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	2.8	2	2.8	3	2.8	From the graph, it shows that the values are consistent as all the values start from 2.8 μm.
Reading	Surface Roughness (μm)								
1	2.8								
2	2.8								
3	2.8								
Average Sample A  <table border="1"><caption>Data for Average Sample A</caption><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>3.8</td></tr><tr><td>2</td><td>5.0</td></tr><tr><td>3</td><td>2.8</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	3.8	2	5.0	3	2.8	The graph displays irregular consistency as the gap between each of the average value is large. The average value at point 2 is the highest as compared to the other points. The error bar displays big difference, which also means the average values of surface roughness is uncertain.
Reading	Surface Roughness (μm)								
1	3.8								
2	5.0								
3	2.8								
Sample B at Point 1  <table border="1"><caption>Data for Sample B at Point 1</caption><thead><tr><th>Reading</th><th>Surface Roughness (μm)</th></tr></thead><tbody><tr><td>1</td><td>5.0</td></tr><tr><td>2</td><td>5.2</td></tr><tr><td>3</td><td>5.1</td></tr></tbody></table>	Reading	Surface Roughness (μm)	1	5.0	2	5.2	3	5.1	<i>Position B</i> The surface roughness values from Reading 2 and Reading 3 have small difference while the value from the first reading is the lowest for this point.
Reading	Surface Roughness (μm)								
1	5.0								
2	5.2								
3	5.1								

Sample B at Point 2

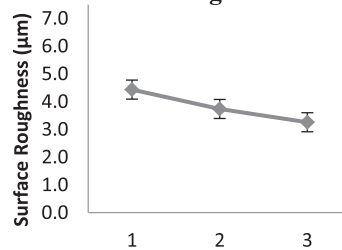
Graph has the lowest surface roughness value for 70% of filler and the value from Reading 1 is the lowest while the values at Reading 2 and Reading 3 are consistent.

Sample B at Point 3

The data produces a consistent graph plot since there is small gap between all of the surface roughness values.

Average Sample B

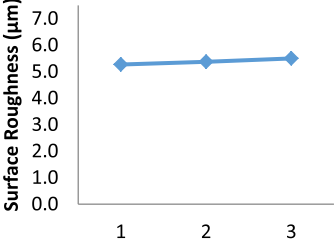
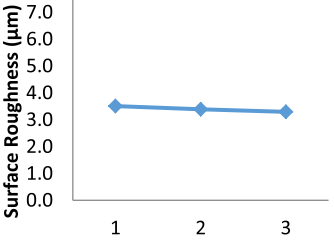
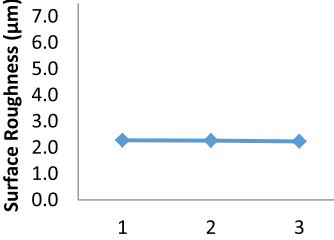
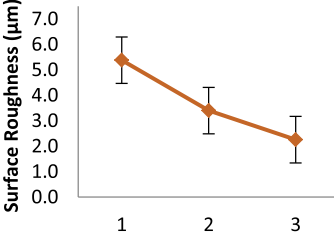
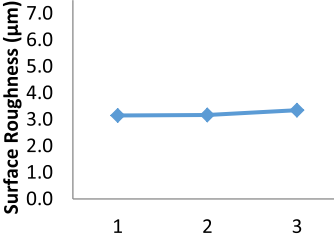
The graph exhibits irregular consistency as the gap between each of the average value is large. The average value at point 2 is the lowest as compared to the other points. The error bars show long dimension, which means that the concentration of calculated average values is low.

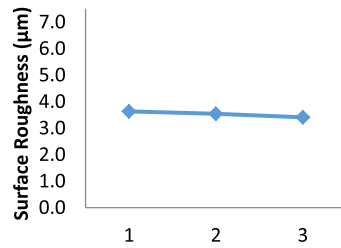
Total Average A & B

Total average at positions A & B

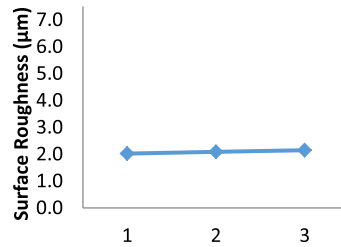
The total average values are gradually decreasing across all of three points, which indicates the presence of irregular consistency. The error bar appears to be small that means the total average values of surface irregularities on the sample are slightly certain.

Table 10 Analysis of vertical results for 80% of filler

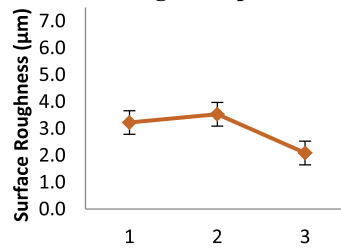
Vertical results	Analysis
Sample A at Point 1 	<i>Position A</i> Through the graph, the data can be seen gradually increases across all of the readings with small gap between each readings.
Sample A at Point 2 	The surface roughness values from Reading 2 and Reading 3 produce consistent graph plot while the value at Reading1 is the highest at this point.
Sample A at Point 3 	The graph exhibits consistency between all of the values of surface roughness across all of the readings.
Average Sample A 	Ra is gradually decreasing across all of three points, which indicates the presence of irregular consistency. The error bar appears to be large it is caused by the low concentration of calculated average values plus the difference between the highest and the lowest average value is high, 2.13 µm.
Sample B at Point 1 	<i>Position B</i> At Reading 1 and Reading 2, the data shows consistency but the data increases from Reading 3, which shows obvious gap between the values from Reading 2 and Reading 3.

Sample B at Point 2

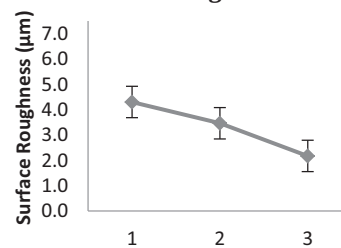
From the graph, the surface roughness value at Reading 1 is the highest and the values gradually decrease across all of the readings with small difference.

Sample B at Point 3

The surface roughness value at Reading 3 is the highest as compared to other two points that have small difference in value between each other.

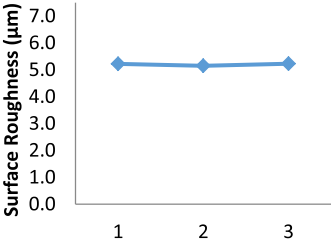
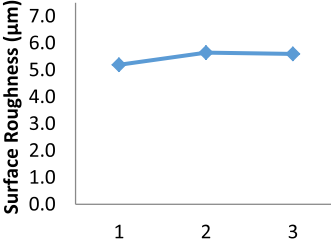
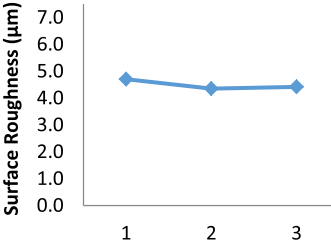
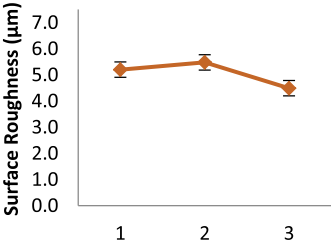
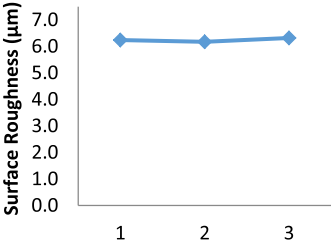
Average Sample B

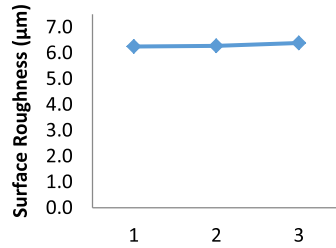
The graph displays irregular consistency as the difference between each of the value is large. The average value at point 3 is the lowest as compared to the other points. The error bar appears to be short that means the average values surface irregularities on the sample are slightly certain.

Total Average A & B**Total average at positions A & B**

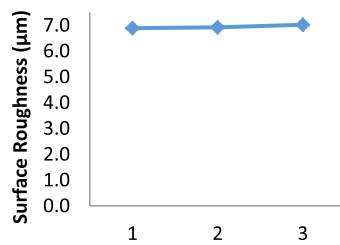
The total average values are gradually decreasing across the points with the range of gap 0.8–1.3 μm. The error bar appears to be large that means the total average values of surface irregularities is uncertain.

Table 11 Analysis of vertical results for 90% of filler

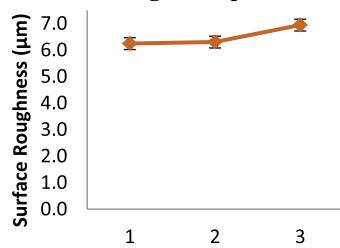
Vertical Results	Analysis
Sample A at Point 1 	<i>Position A</i> The surface roughness values from Reading 1 and Reading 3 are consistent while the value at Reading 2 is a bit decreasing.
Sample A at Point 2 	Graph shows that the surface roughness values from Reading 2 and Reading 3 are consistent while the value at Reading 1 has obvious difference from the other values.
Sample A at Point 3 	From the graph, the surface roughness value at Reading 1 is the highest while the values from Reading 2 and Reading 3 display stable consistency.
Average Sample A 	Each of average values has small difference between all of the points and the average value at point 2 being the highest value. The error bar appears to be small that means the surface irregularities on the sample are slightly consistent.
Sample B at Point 1 	<i>Position B</i> The total Ra values from Reading 1 and Reading 3 exhibit consistency while the value at Reading 2 is the lowest among them.

Sample B at Point 2

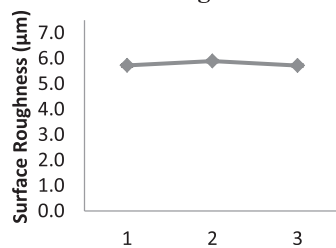
From the graph, the surface roughness values from Reading 3 shows the highest value of surface roughness while at Reading 1 and Reading 2, their values are consistent

Sample B at Point 3

The Ra values from Reading 1 and Reading 2 are consistent while at Reading 3 shows the highest value of surface roughness.

Average Sample B

The average values at point 1 and point 2 show consistency while the average values at point 3 being the highest among all of the points. The error bar appears to be small that means the surface irregularities of the sample are slightly certain.

Total Average A & B

Total average at positions A & B

From the graph, it shows that the total Ra values at each point have small difference between each other. The error bar can hardly be seen, which explains that there is slightly small difference between the total average values and the concentration of calculated average values is high.

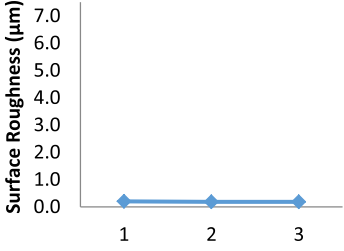
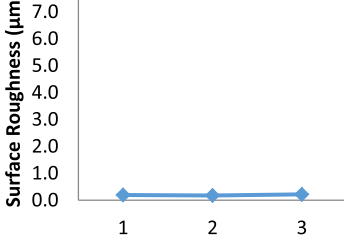
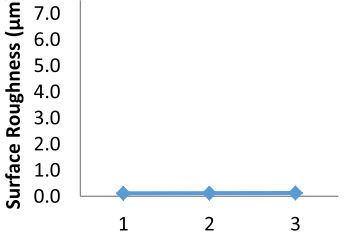
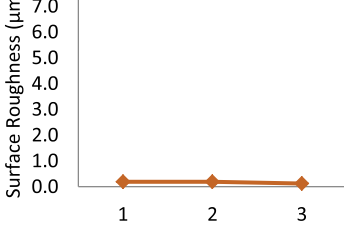
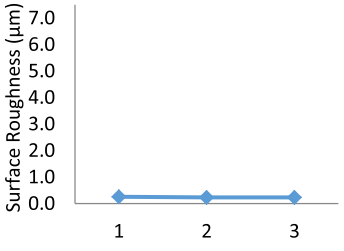
Surface Roughness in Horizontal Direction

Each of the data is translated into the graph that represents three types of relation; relationship between surface roughness and number of measurement taken on the same spot, relationship between Ra and point of measurement and relationship between

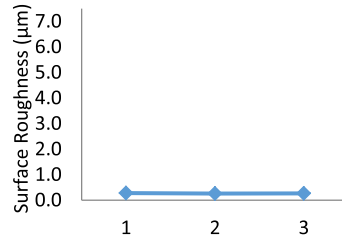
Table 12 Horizontal direction results

% of Filler	Position	Surface roughness (μm)								
		Point 1	Average	Total average A & B	Point 2	Average	Total average A & B	Point 3	Average	Total average A & B
10	A	0.202	0.189	0.215	0.189	0.190	0.228	0.115	0.121	0.121
		0.181			0.170			0.124		
		0.184			0.212			0.125		
	B	0.256	0.241		0.277	0.266		0.120	0.120	
		0.235			0.258			0.121		
		0.233			0.264			0.118		
20	A	0.828	0.830	0.943	1.450	1.450	1.507	1.116	1.116	1.135
		0.825			1.454			1.122		
		0.836			1.445			1.111		
	B	1.058	1.056		1.554	1.565		1.151	1.154	
		1.052			1.572			1.161		
		1.059			1.569			1.149		
30	A	1.288	1.327	0.952	1.597	1.568	1.506	1.155	1.149	1.116
		1.343			1.603			1.136		
		1.349			1.503			1.155		
	B	0.586	0.578		1.439	1.444		1.078	1.084	
		0.575			1.436			1.092		
		0.572			1.456			1.082		
40	A	0.493	0.497	0.469	0.222	0.221	0.228	0.336	0.339	0.340
		0.496			0.218			0.349		
		0.501			0.224			0.333		
	B	0.437	0.441		0.230	0.234		0.337	0.340	
		0.444			0.239			0.339		
		0.441			0.234			0.343		
50	A	0.385	0.373	0.502	0.458	0.463	0.439	1.587	1.595	1.071
		0.367			0.459			1.606		
		0.366			0.473			1.591		
	B	0.754	0.631		0.367	0.415		0.530	0.547	
		0.539			0.405			0.556		
		0.601			0.472			0.554		
60	A	4.108	4.185	4.238	3.228	3.218	3.546	2.840	2.774	3.186
		4.213			3.209			2.713		
		4.235			3.218			2.769		
	B	4.299	4.291		3.865	3.873		3.592	3.597	
		4.314			3.887			3.596		
		4.261			3.866			3.604		
70	A	3.502	3.510	3.516	4.666	4.686	4.393	4.428	4.464	4.132
		3.507			4.691			4.491		
		3.521			4.700			4.473		
	B	3.535	3.523		4.091	4.101		3.735	3.800	
		3.531			4.117			3.744		
		3.502			4.095			3.920		
80	A	5.266	5.287	4.335	3.212	3.215	3.366	3.849	3.859	3.740
		5.226			3.221			3.855		
		5.370			3.213			3.873		
	B	3.409	3.382		3.541	3.516		3.628	3.621	
		3.349			3.509			3.620		
		3.387			3.499			3.614		
90	A	4.288	4.194	4.765	4.948	5.076	5.279	5.018	5.026	5.641
		4.212			5.166			5.151		
		4.083			5.114			4.910		
	B	5.288	5.335		5.465	5.483		6.240	6.255	
		5.335			5.493			6.248		
		5.382			5.490			6.276		

Table 13 Analysis of horizontal results for 10% of filler

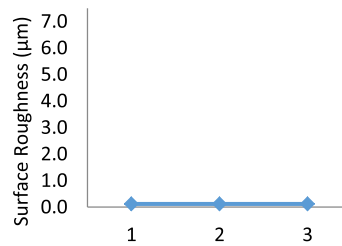
Horizontal Results	Analysis
Sample A at Point 1 	<i>Position A</i> Graph has low surface roughness that is in the range of 0.18–0.25 μm, which means that the result has stable consistency.
Sample A at Point 2 	The graph illustrates low surface roughness where the range is 0.18–0.25 μm, similarly to the previous point.
Sample A at Point 3 	This area has the lowest surface roughness that is in range of 0–0.15 μm, which means that it has the smoothest surface.
Average Sample A 	At point 3, Ra between three points is the lowest as compared to the other two points, but the sample still has smooth surface. The error bar appears to be short since the difference between the highest and the lowest values at each point are 0.021 μm, 0.042 μm and 0.010 μm.
Sample B at Point 1 	<i>Position B</i> The graph illustrates low surface roughness with small gap of value between the times of data reading.

Sample B at Point 2



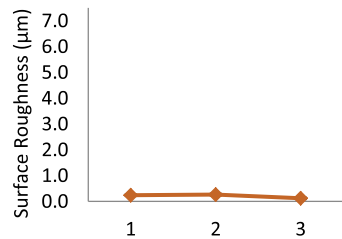
Graph has the highest surface roughness value as compared to other points in both positions, but in consistent range.

Sample B at Point 3



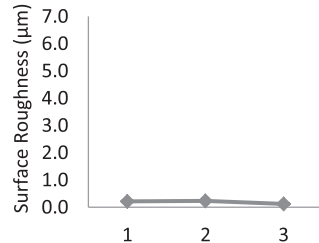
Graph has the lowest surface roughness value as compared to the value in this position. At third reading when the data is taken, the value slightly decreases.

Average Sample B



At the first and second points the data is taken, the Ra value is consistent while at the third point, the value decreases, but the sample is still in homogenous solution since the gap value is small. The error bar can barely be seen since the difference between the highest and the lowest values at each point is not exceeding 0.03 μm.

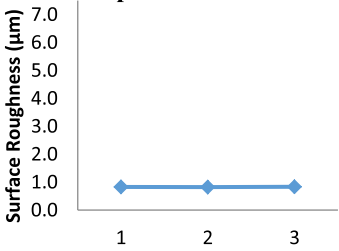
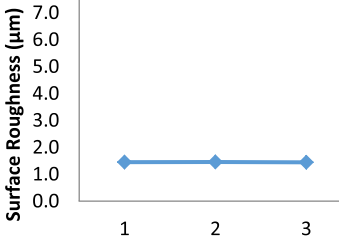
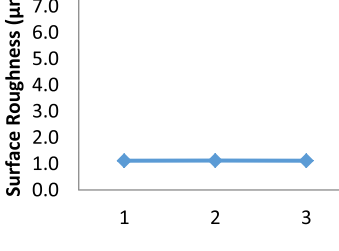
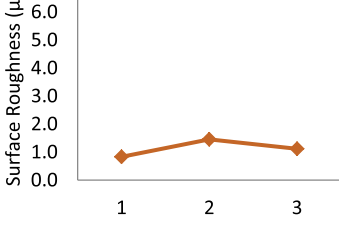
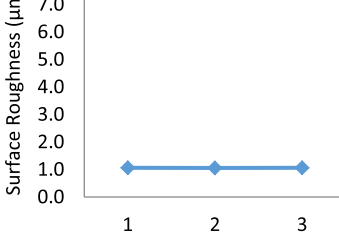
Total Average A & B



Total average at positions A & B

At point 1 and 2, the total Ra is consistent while at point 3, it decreases in value but in small gap, which describes that the sample is in homogenous solution. The error bar can barely be seen, which proves that the total average values are more certain.

Table 14 Analysis of horizontal results for 20% of filler

Horizontal Results	Analysis
Sample A at Point 1  Surface Roughness (μm) 1 2 3	<i>Position A</i> This area has the lowest surface roughness that is in range of 0.5–1 μm, which means that it has the smoothest surface.
Sample A at Point 2  Surface Roughness (μm) 1 2 3	Graph consists of range of surface roughness around 1.45 μm with consistent gap, which is the highest in this position. Ra value rapidly increases as compared to the previous point.
Sample A at Point 3  Surface Roughness (μm) 1 2 3	This area has lower surface roughness as compared to the data at Point 2 with small gap between each data that proves the result has stable consistency.
Average Sample A  Surface Roughness (μm) 1 2 3	At point 1, the Ra between three points is the lowest as compared to the other two points, but the sample still has smooth surface. The error bar can barely be seen that means the surface irregularities on the sample are slightly consistent.
Sample B at Point 1  Surface Roughness (μm) 1 2 3	<i>Position B</i> It has the lowest surface roughness value as compared to the value in this position with small gap of value between the times of data reading.

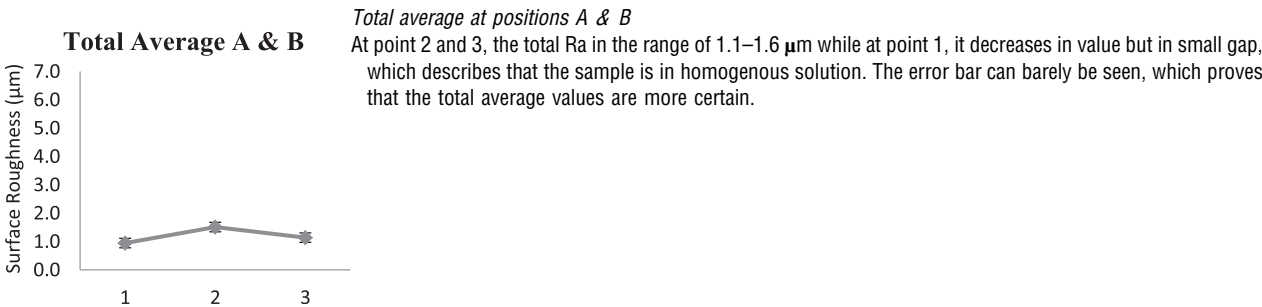
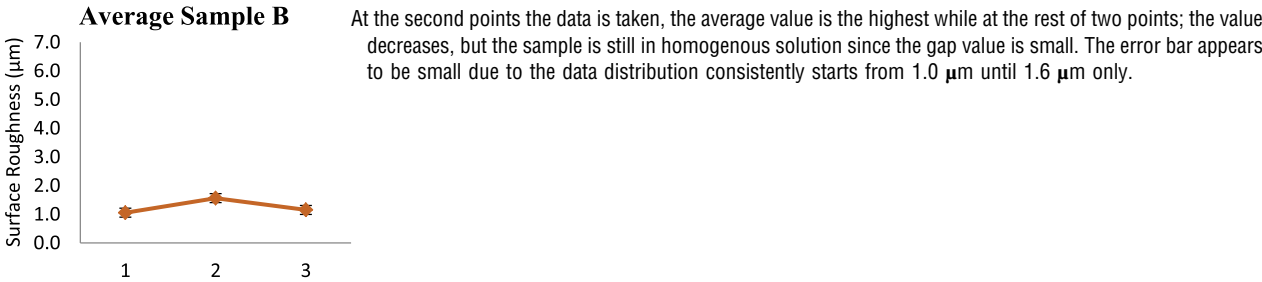
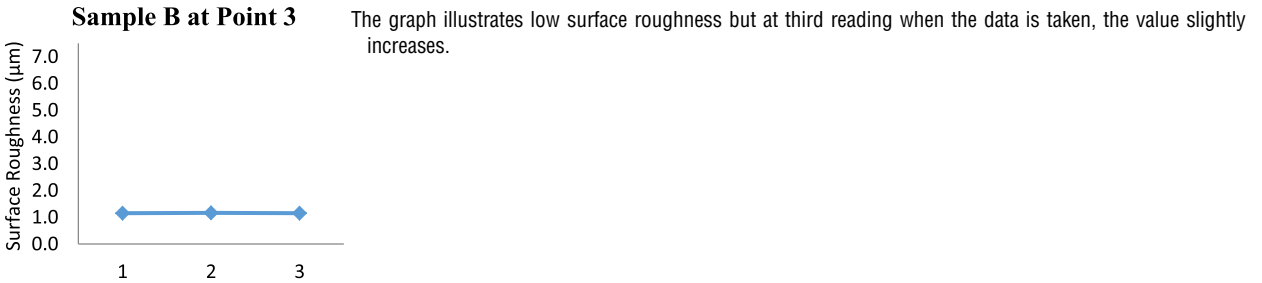
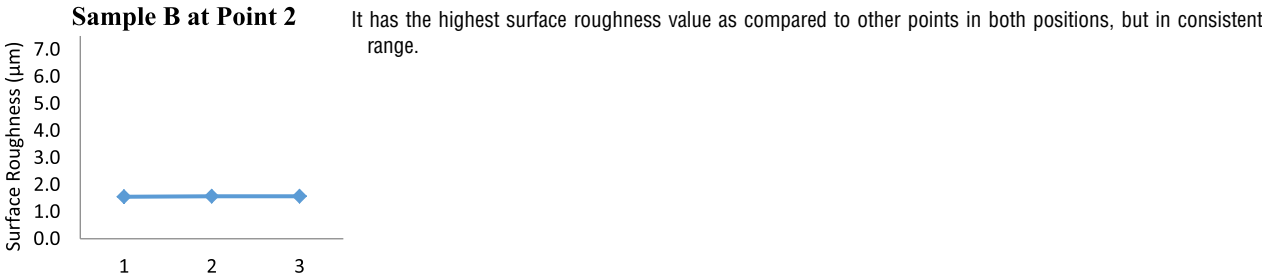
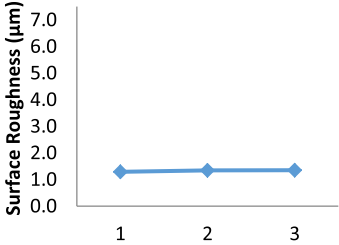
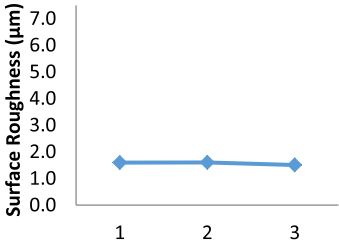
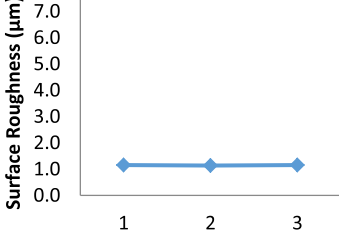
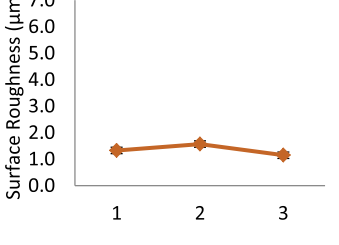
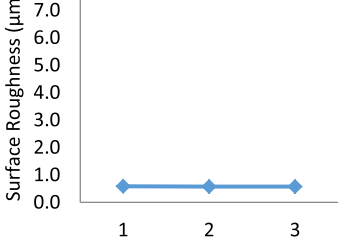


Table 15 Analysis of horizontal results for 30% of filler

Horizontal Results	Analysis
Sample A at Point 1 	<i>Position A</i> It has surface roughness that is in range of 1.28–1.35 μm, which means that the result has stable consistency as it has small gap between the data.
Sample A at Point 2 	The graph illustrates low surface roughness where the range is 1.5–1.6 μm, but it increases as compared to the previous point.
Sample A at Point 3 	This area has the lowest surface roughness that is in the range of 1.13–1.16 μm, which means that it still has the smoothest surface.
Average Sample A 	At point 3, the average of surface roughness between three points is the lowest as compared to the other two points, but the sample still has smooth surface. The error bar appears to be small due to the data distribution consistently starts in the range of 1.13 μm until 1.61 μm.
Sample B at Point 1 	<i>Position B</i> It has the lowest surface roughness value as compared to other points in both positions, but in consistent range.

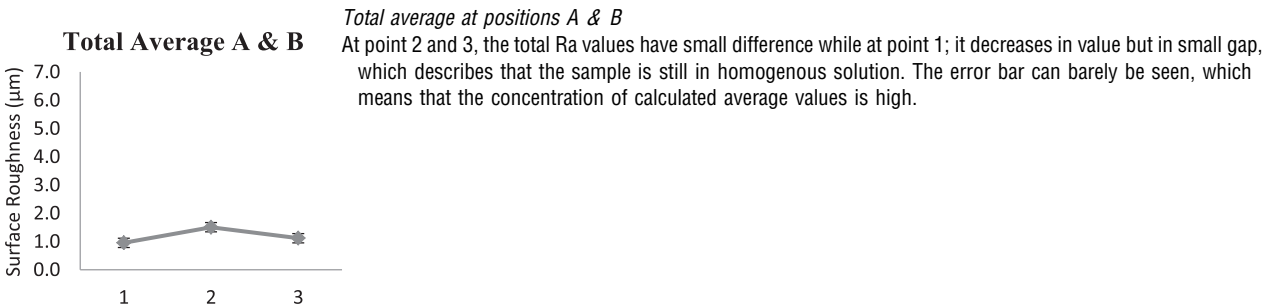
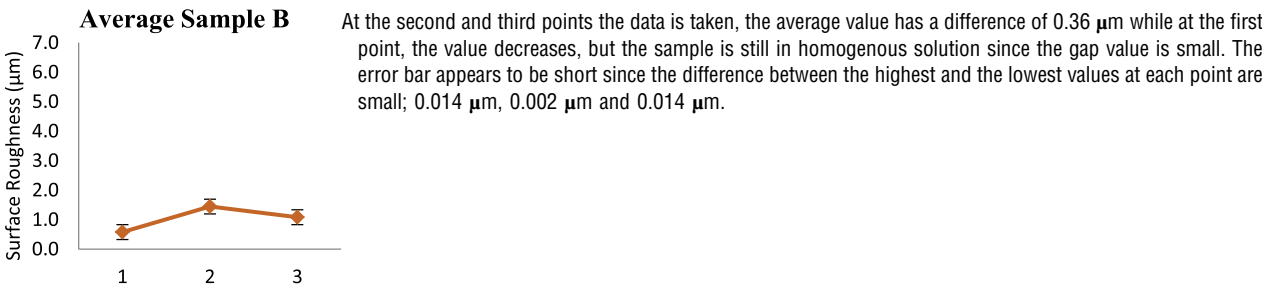
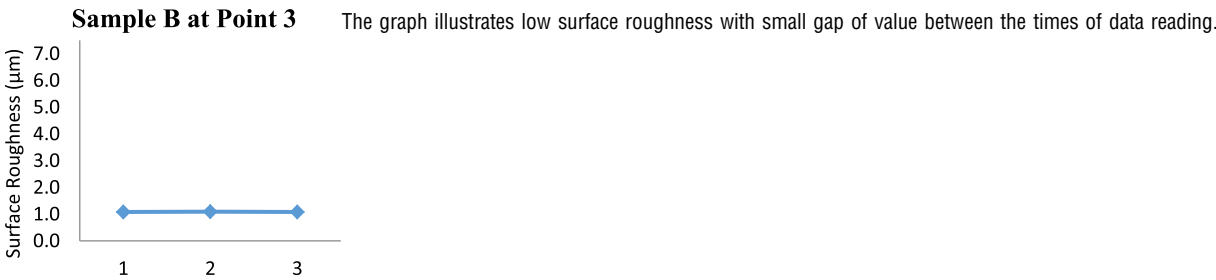
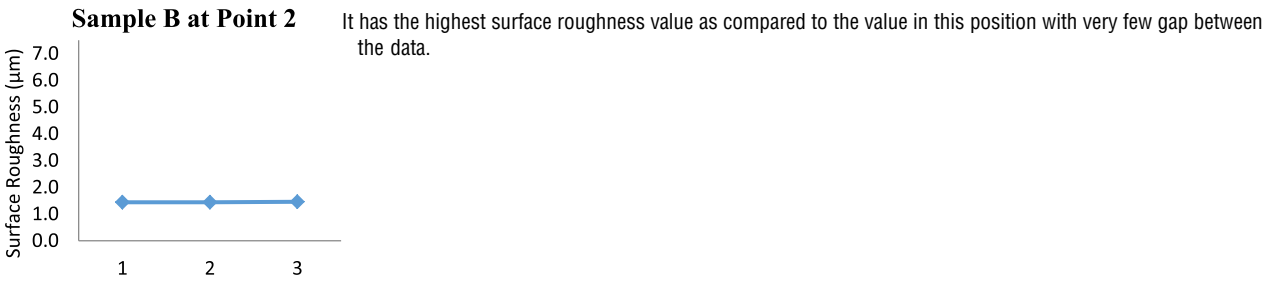
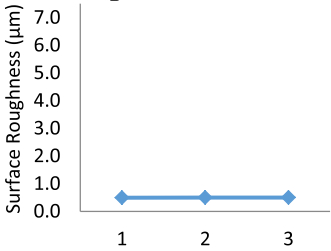
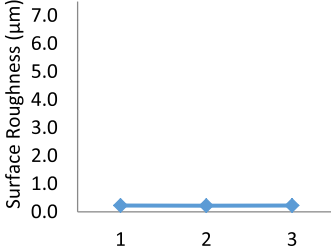
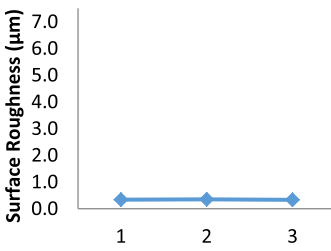
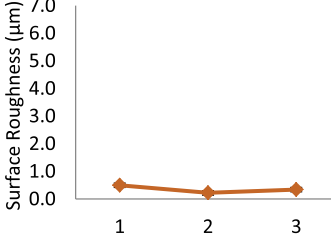
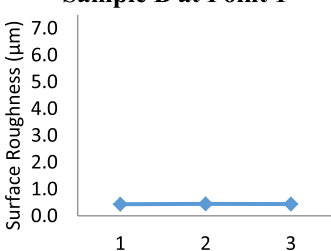


Table 16 Analysis of horizontal results for 40% of filler

Horizontal Results	Analysis
Sample A at Point 1  Surface Roughness (μm) 1 2 3	<i>Position A</i> The value of surface roughness at this point is the highest for 40% of filler, which ranges up to 0.5 μm.
Sample A at Point 2  Surface Roughness (μm) 1 2 3	The graph exhibits there is small increasing of value at Reading 3 as compared to two other remaining readings.
Sample A at Point 3  Surface Roughness (μm) 1 2 3	The data presents up to no difference among all of the three readings since their values are around 0.3 μm.
Average Sample A  Surface Roughness (μm) 1 2 3	The average value of surface roughness is the highest at point 1 but the average value starts to decrease at point 2 and point 3. The error bar can hardly be seen, which proves that there is small difference between the average values.
Sample B at Point 1  Surface Roughness (μm) 1 2 3	<i>Position B</i> Highest surface roughness with small gap of value between the times of data reading.

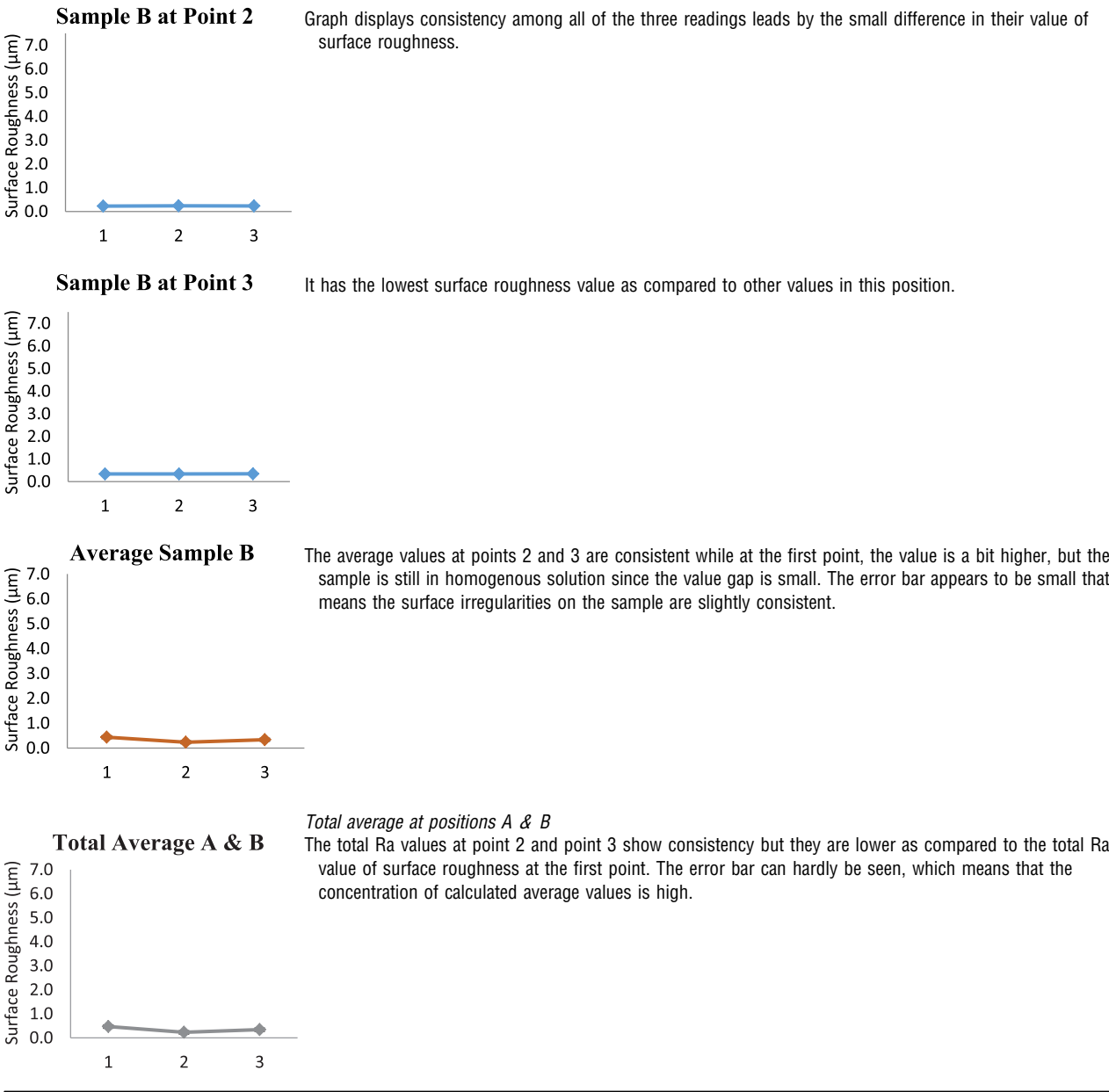
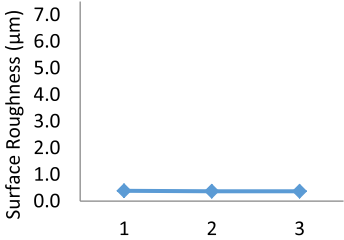
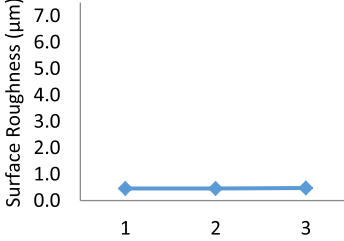
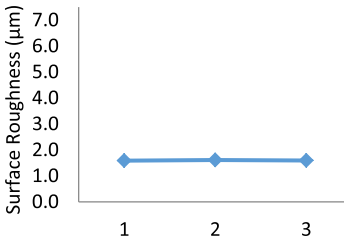
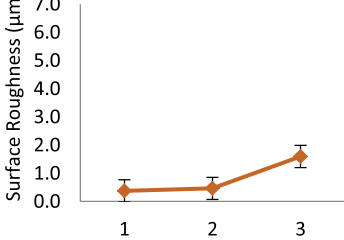
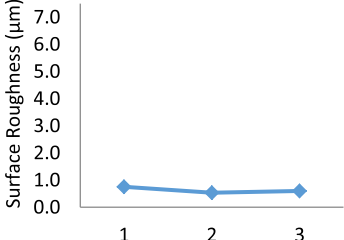


Table 17 Analysis of horizontal results for 50% of filler

Horizontal Results	Analysis
Sample A at Point 1  Surface Roughness (μm) 1 2 3	<i>Position A</i> The graph shows a stable consistency among the values since the difference of surface roughness show no difference.
Sample A at Point 2  Surface Roughness (μm) 1 2 3	The graph also encounters similar situation as in the previous graph where the data being displayed has small difference.
Sample A at Point 3  Surface Roughness (μm) 1 2 3	The values from Reading 1 and Reading 2 are consistent but at Reading 3, the value is slightly increasing.
Average Sample A  Surface Roughness (μm) 1 2 3	From Point 3, the increasing average value is obvious while the average values at Point 1 and Point 2 are consistent. The error bar appears to be obvious as the difference between the highest and the lowest values at each point are small; 0.019 μm, 0.015 μm and 0.015 μm.
Sample B at Point 1  Surface Roughness (μm) 1 2 3	<i>Position B</i> From the graph, the surface roughness value at Reading 1 is the highest while the values from Reading 2 and Reading 3 display stable consistency.

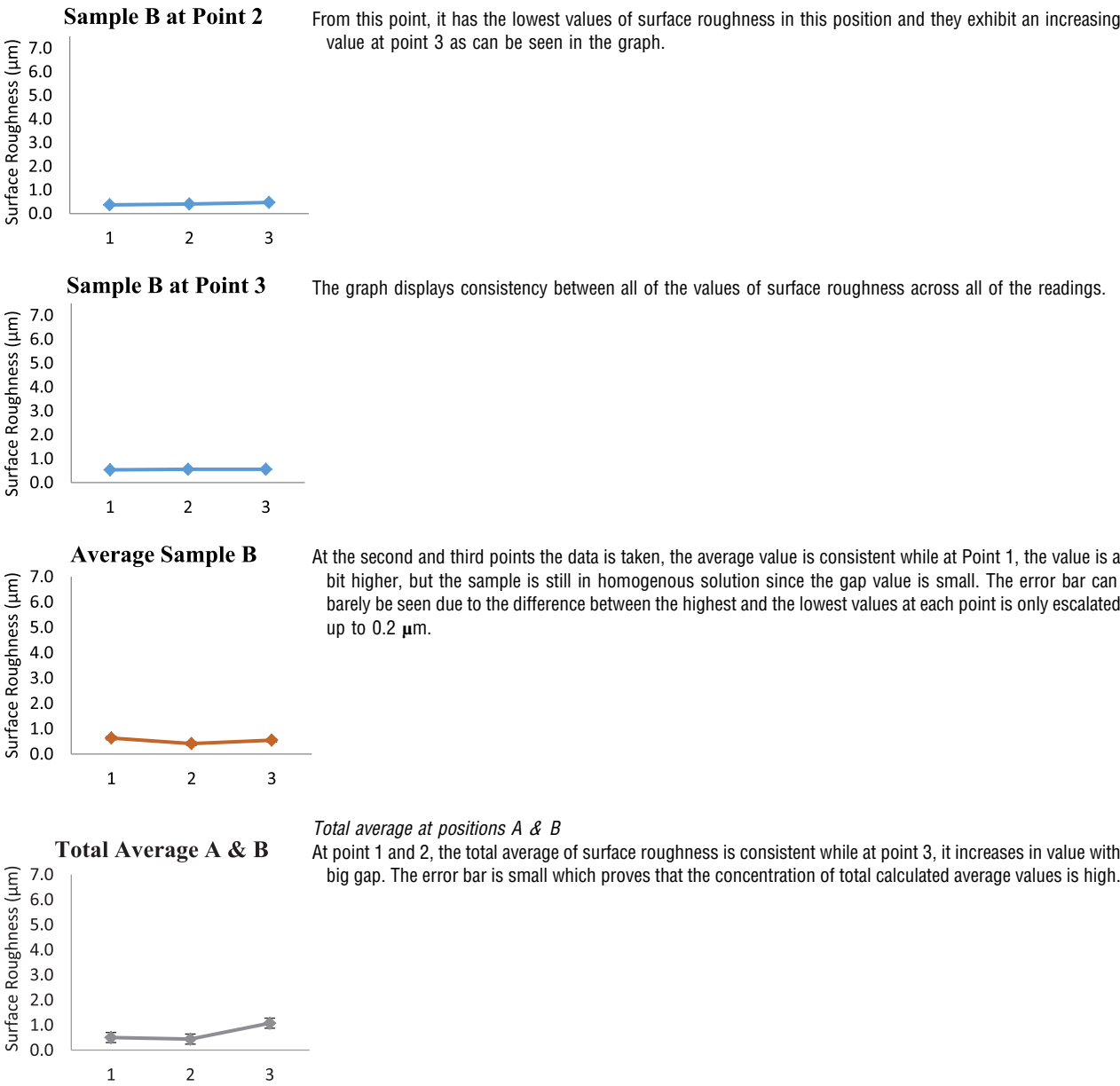
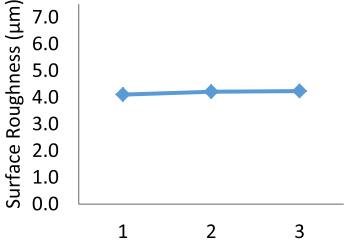
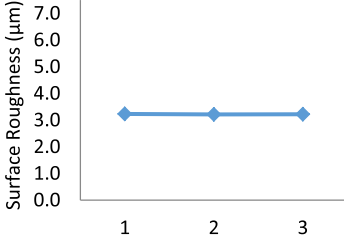
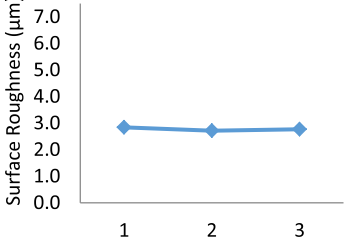
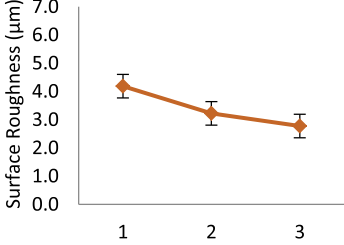
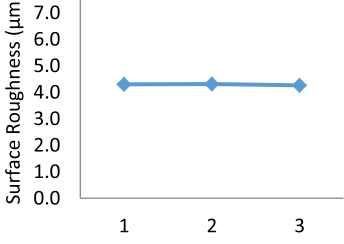


Table 18 Analysis of horizontal results for 60% of filler

Horizontal Results	Analysis
Sample A at Point 1  Surface Roughness (μm) 1 2 3	<i>Position A</i> The values rapidly increasing from the previous percentage of fillers where they start from 2 μm and above.
Sample A at Point 2  Surface Roughness (μm) 1 2 3	The graph displays stable consistency since their range is consistent that is around 3.2 μm.
Sample A at Point 3  Surface Roughness (μm) 1 2 3	The value from Reading 1 is a bit higher as compared to the values from Reading 2 and Reading 3 that are consistent between each other.
Average Sample A  Surface Roughness (μm) 1 2 3	There is no stable consistency among the average values being displayed in the graph as the difference value between the highest and the lowest data is 1.411 μm. The error bar is in obvious dimension since the difference between the highest and the lowest values at each point are 0.127 μm, 0.019 μm and 0.127 μm
Sample B at Point 1  Surface Roughness (μm) 1 2 3	<i>Position B</i> The graph exhibits consistency in the data but the value from Reading 3 is slightly lower than the other values.

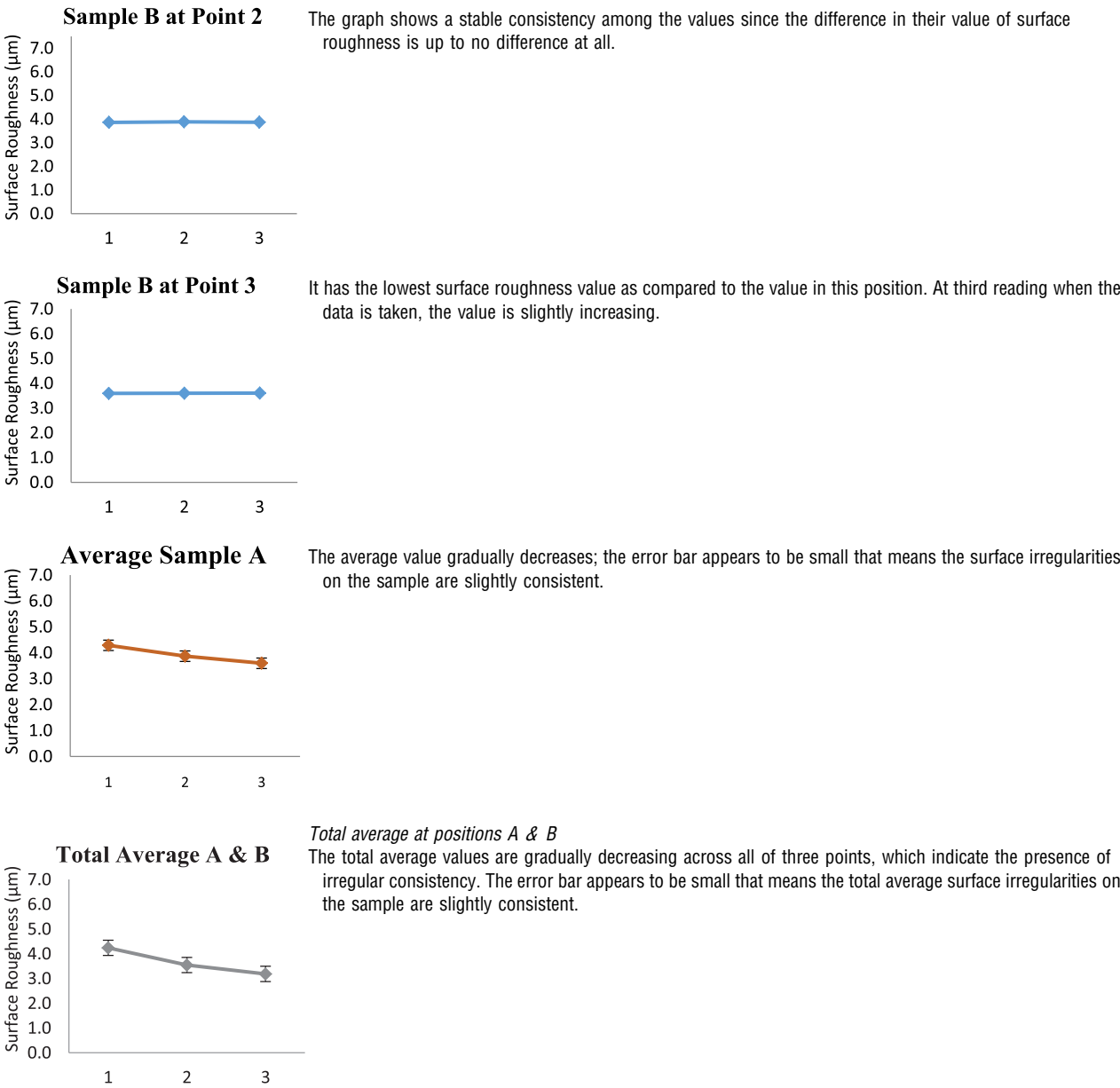
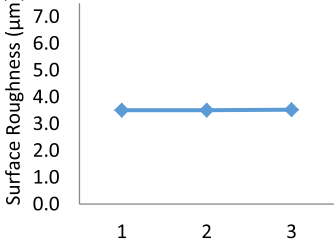
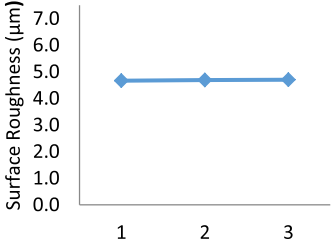
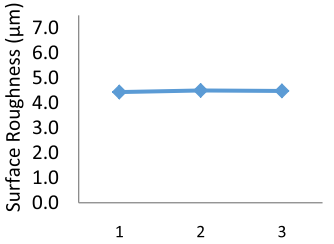
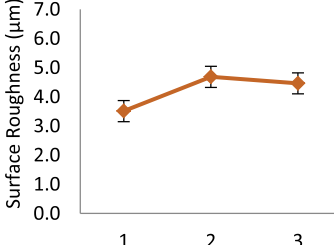
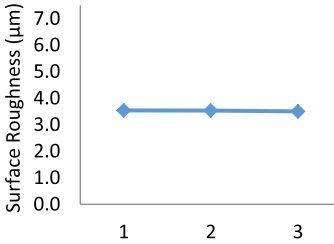


Table 19 Analysis of horizontal results for 70% of filler

Horizontal Results	Analysis
Sample A at Point 1 	<i>Position A</i> From the graph, it shows that the values are consistent as all of the values start from 3.5 μm.
Sample A at Point 2 	Data distribution does not produce obvious inconsistency in the graph as the gap between each data is small.
Sample A at Point 3 	The data produces a consistent graph plot since there is small gap between all of the surface roughness values.
Average Sample A 	The graph displays irregular consistency as the difference between each of the average values is large. The average value at point 1 is the lowest as compared to the other points. The error bar appears to be small, which is caused by the concentration of calculated Ra values is high. The difference between the highest and the lowest average values is low, 0.954 μm.
Sample B at Point 1 	<i>Position B</i> It has the lowest surface roughness value as compared to the value in this position. At third reading when the data is taken, the value slightly increases.

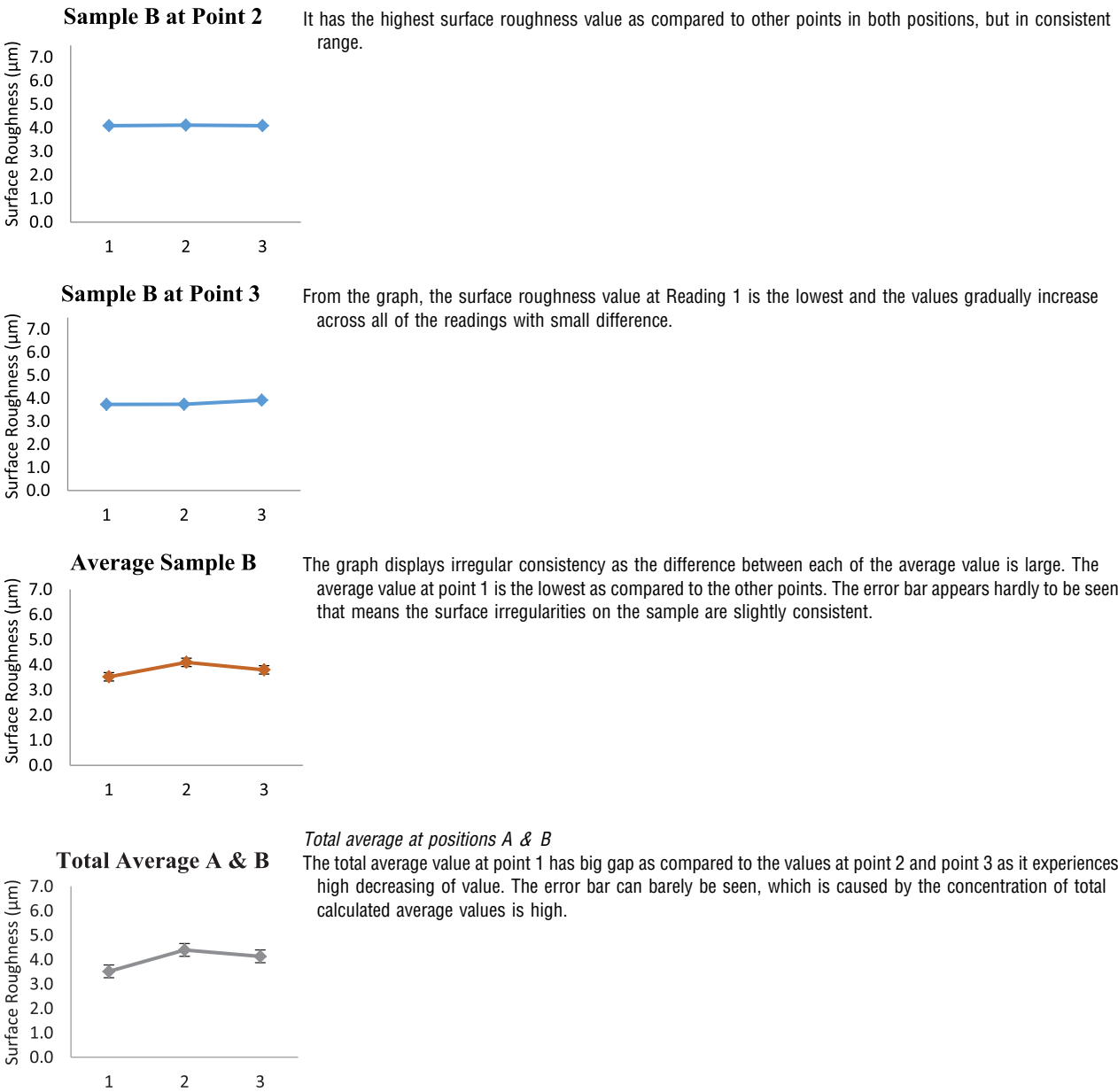
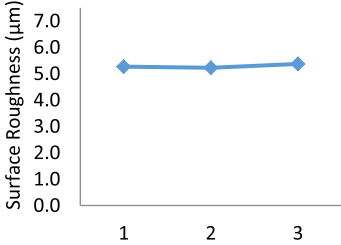
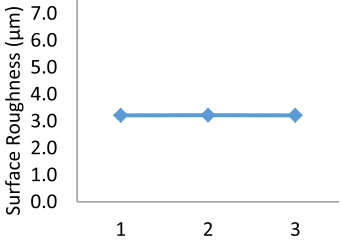
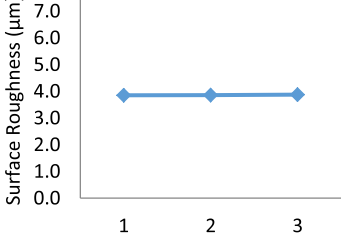
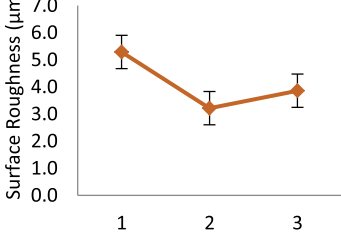
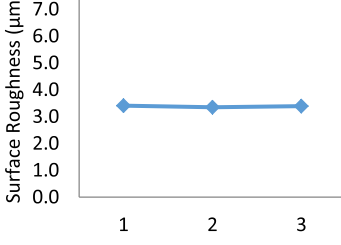
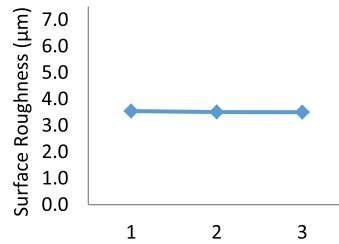


Table 20 Analysis of horizontal results for 80% of filler

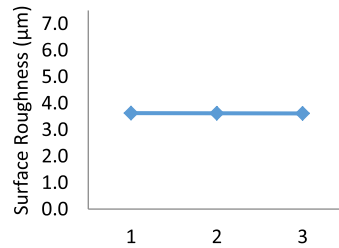
Horizontal Results	Analysis
Sample A at Point 1 	<i>Position A</i> The values from Reading 1 and Reading 2 are consistent but at Reading 3, the value is slightly increasing.
Sample A at Point 2 	It has the lowest surface roughness value as compared to the value in this position. At second reading when the data is taken, the value slightly increases.
Sample A at Point 3 	The graph shows stable consistency since their range is consistent that is around 3.8 μm.
Average Sample A 	The graph exhibits irregular consistency as the gap between each of the average value is large. The average value at point 2 is the lowest as compared to the other points. The error bar appears to be large, which is caused by the concentration of calculated average values is low. The difference between the highest and the lowest average values is high, 2.072 μm.
Sample B at Point 1 	<i>Position B</i> The surface roughness values from Reading 1 and Reading 3 have small difference while the value from the second reading is the lowest for this point.

Sample B at Point 2

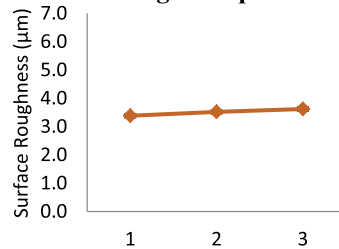
The data produces a consistent graph plot since there is small gap between all of the surface roughness values.

**Sample B at Point 3**

The graph shows a stable consistency among the values since the difference in their value of surface roughness is up to no difference.

**Average Sample A**

The average value gradually increases; the error bar appears barely to be seen that means the surface irregularities on the sample are certain.

**Total Average A & B**

Total average at positions A & B

From the graph; at point 2 and 3, the total average value has small difference while at point 1; it has the highest value but in small gap. The error bar appears to be small since the difference between the highest and the lowest total average values is below 1 μm.

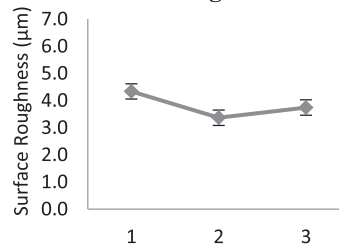
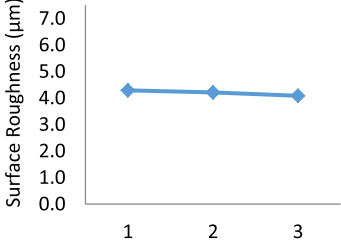
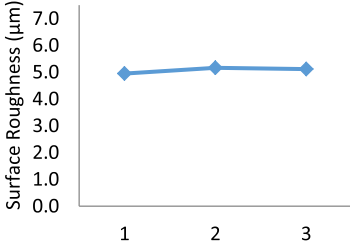
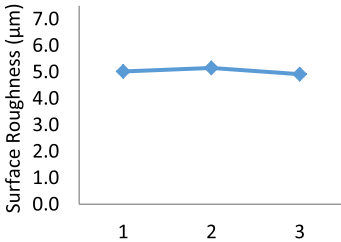
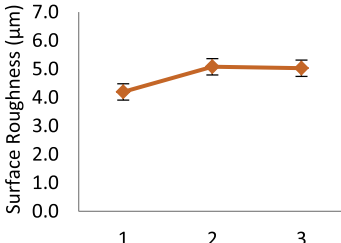
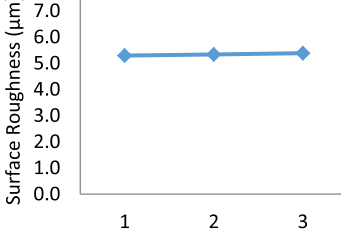
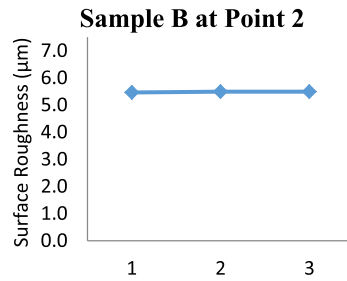
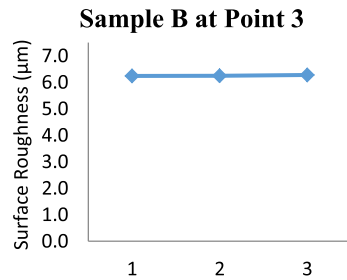


Table 21 Analysis of horizontal results for 90% of filler

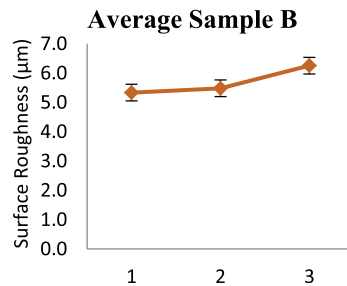
Horizontal Results	Analysis
Sample A at Point 1 	<i>Position A</i> The surface roughness values from Reading 1 and Reading 2 produce consistent graph plot while the value at Reading 3 is slightly lower at this point.
Sample A at Point 2 	The values rapidly increasing from the previous percentage of fillers where they start from 5 µm and above. From the graph, the values at Reading 2 and Reading 3 are consistent while at Reading 1, the value is a bit lower.
Sample A at Point 3 	The value from Reading 3 is the lowest as compared to the values from Reading 1 and Reading 3 that have small gap between each other.
Average Sample A 	Through the graph, Ra starts to increase from Reading 1 to Reading 2 with the difference value of 0.882 µm while the data keeps consistent between the second and third readings. The error bar is in small dimension that is caused by the difference between the highest and the lowest values at each point is only up to 0.25 µm.
Sample B at Point 1 	<i>Position B</i> The graph displays consistency between all of the values of surface roughness across all of the readings with slight increase at Reading 3.



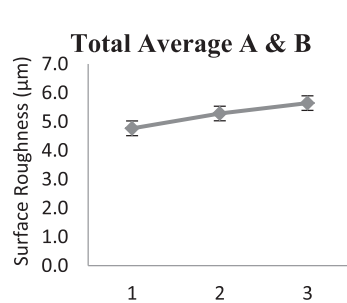
From the graph, it shows that the values are consistent as all of the values start from 5.4 μm .



It has the highest surface roughness value for 90% of filler and the value keeps in stable consistency as their values start from 6.2 μm and above.



Average values from points 1 and 2 have small difference but the average value at point 3 increases thus, being the highest value. The error bar appears to be short due to the difference between the highest and the lowest values at each point is only escalated up to 0.042 μm .



Total average at positions A & B

Total Ra value keeps increasing across the three points as shown in the graph. The error bar appears to be small that means the total average values of surface irregularities on the sample are certain and the concentration of calculated average values is high.

total Ra and measurement points at both positions. The overall results for horizontal is shown in [Table 12](#). In addition, [Table 13](#) shows the results for 10% filler, [Table 14](#) for 20% filler, [Table 15](#) for 30% filler, [Table 16](#) for 40% filler, [Table 17](#) for 50% filler, [Table 18](#) for 60% filler, [Table 19](#) for 70% filler, [Table 20](#) for 80% filler and [Table 21](#) for 90% filler, respectively.

From the table of results in both directions, the values of surface roughness for the sample of 10% of filler until 50% of filler are below 1.9 μm with the lowest value of Ra in vertical direction is 0.091 μm while in horizontal direction is 0.115 μm . The highest value of Ra from 10% of filler until 50% of filler in vertical direction is 1.803 μm and for the horizontal direction is 1.606 μm .

For 60% and the rests of the sample, their values of surface roughness in both directions surpass 2.0 μm with the highest value of Ra is 7.017 μm in vertical direction and 6.276 μm in horizontal direction.

In vertical direction, graphs that show stable consistency are resulted from 10% of filler up to 50% of filler including 90% of filler. The graph with the most stable consistency is exhibited by the 50% of filler since there is not much difference between the taken data. The rests of the sample from 60% to 80% of filler display irregular consistency among the recorded data. Large error is detected in the graphs that indicating the concentration of calculated average values is low, thus the average value is uncertain.

For horizontal direction, graphs that illustrate the stable consistency are contributed from 10% to 70% of filler including 90% of filler. The error bar from the graphs of average values and total values of Ra are small or can barely be seen, which prove that the concentration of calculated average values is high. Thus, the average value is certain. Graph of average and total average values of

Ra at 80% of filler display the most obvious difference in the error bar as the error bar is long. It means that the surface irregularities on the sample are not consistent.

From all of the graphs that had been constructed, they attribute that the samples with lower filler percentage have consistent Ra and smooth surface. Meanwhile, for the samples with high percentage of filler have inconsistent surface irregularities that contribute to rougher surface.

Conclusion

Through the formulation of ink that has been done before, all of the processes including mixing, printing and curing can be performed to fabricate the ink on the substrates in house. After the fabrication has been carried out, the behaviour of conductive ink is investigated through various tests and one of them is surface roughness. Based on the results, it can be concluded that if the surface texture is the highlight of the subject, it can be summarized from the results of average value of surface roughness. They show that the samples with lower filler percentage have consistent average value and smooth surface. Meanwhile, for the samples with high percentage of filler have inconsistent surface irregularities that contribute to rougher surface.

References

- Allen, M.L., Aronniemi, M., Mattila, T., *et al.*, 2008. Electrical sintering of nanoparticle structures. *Nanotechnology* 19 (17), 175201.
- Burton, J., 2008. A primer on UV-Curable Inkjet Inks.
- Gökkaya, H., Nalbant, M., 2007. The effects of cutting tool coating on the surface roughness of AISI 1015 steel depending on cutting parameters. *Turkish Journal of Engineering and Environmental Sciences* 30 (5), 307–316.
- Ikeda, O., Watanabe, Y., Itoh, F., 2007. Corrosion measurement of a conductive paste and anisotropic conductive adhesive films. In: *Proceedings of the Polytronic 2007, 6th International Conference on Polymers and Adhesives in Microelectronics and Photonics*, 2007, (pp. 77–80). IEEE.
- Joshi, S.S., 2011. Evaluation of Silver/Graphite Ink Blends for Use in Printed Electronics.
- Kim, D., Moon, J., 2005. Highly conductive ink jet printed films of nanosilver particles for printable electronics. *Electrochemical and Solid-State Letters* 8 (11), J30–J33.
- Maattanen, N.A., Ihalainen, P., Bollström, R., Toivakka, M., Peltonen, J., 2010. Wetting and print quality study of an inkjet-printed poly (3-hexylthiophene) on pigment coated papers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 367 (1–3), 76–84.
- Moscicki, A., Felba, J., Sobierajski, T., *et al.*, 2005. Electrically conductive formulations filled nano size silver filler for ink-jet technology. In: *Proceedings of the Polytronic 2005, 5th International Conference on Polymers and Adhesives in Microelectronics and Photonics*, Polytronic, 2005, (pp. 40–44). IEEE.
- Nash, C., Spiesschaert, Y., Amarandei, G., *et al.*, 2015. A comparative study on the conductive properties of coated and printed silver layers on a paper substrate. *Journal of Electronic Materials* 44 (1), 497.
- Perelaer, J., De Laat, A.W., Hendriks, C.E., Schubert, U.S., 2008. Inkjet-printed silver tracks: low temperature curing and thermal stability investigation. *Journal of Materials Chemistry* 18 (27), 3209–3215.
- Samano, A., 2017. Measurements of conductive film (Doctoral dissertation, Brunel University London).

Further Reading

- Chen, S.P., Chiu, H.L., Wang, P.H., Liao, Y.C., 2015. Inkjet printed conductive tracks for printed electronics. *ECS Journal of Solid State Science and Technology* 4 (4), P3026–P3033.
- Maissel, L.I., Glang, R., 1970. *Handbook of thin film technology*. Maissel, L.I. (Ed.), 1970. New York: McGraw-Hill.
- Merilampi, S., Björninen, T., Haukka, V., *et al.*, 2010. Analysis of electrically conductive silver ink on stretchable substrates under tensile load. *Microelectronics Reliability* 50 (12), 2001–2011.

Polymer Single-Screw Extrusion With Metal Powder Reinforcement

Rupinder Singh, N Singh, and P Bedi, Guru Nanak Dev Engineering College, Ludhiana, India
IPS Ahuja, Punjabi University Patiala, Patiala, India

© 2016 Elsevier Inc. All rights reserved.

This is a reproduction of R. Singh, N. Singh, P. Bedi, I.P.S. Ahuja, Polymer Single-Screw Extrusion With Metal Powder Reinforcement, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2016, doi:10.1016/B978-0-12-803581-8.04161-8.

Introduction

After two decades of research and development, the additive manufacturing (AM) industry has started to grow with new methods, technologies, and applications (Wohlers, 2007). In addition to the different AM techniques, preparation of filament materials for AM is also gaining great attention from researchers. Many methods are being used in today's industry for the preparation of filament (such as screw extrusion, direct extrusion, drawing, etc.). Most researchers have a significant inclination toward using screw extrusion for preparation of filament for AM because the single-screw extruder has wide applications in the polymer processing industry (Campbell *et al.*, 2001). However, single-screw and twin-screw extrusion are available for material processing (Campbell and Spalding, 2013). Some researchers have used hemp fiber in HDPE to improve mechanical properties. Also, some studies have reported the use of carbon fiber (CF), glass fibers, wood flour, sand, natural fibers, aluminum powder, aluminum oxide, and carbon nanotubes as reinforcements (Herrera-Franco *et al.*, 1997; Adhikary *et al.*, 2008; Lu and Oza, 2013; Jen and Huang, 2014; Oliveux *et al.*, 2015; Yildirim *et al.*, 2015) to improve properties.

Furthermore, fused deposition modeling (FDM) was used in some studies to create specific dimensions for wear testing (Singh and Singh, 2016). As reported in this study, initially ABS was used as filament wire in the FDM machine. However, ABS has its own disadvantage in terms of strength and hardness (Zhong *et al.*, 2001), which were improved by reinforcement in the ABS matrix. In the present work, an effort has been made to develop an alternate filament for FDM with hybrid reinforcement of SiC and Al₂O₃ with Nylon-6 as matrix material to improve the mechanical properties of alternate filament wire.

Screw Extrusion

Extrusion methods are widely used for processing polymers and composites containing them, agricultural raw materials, food, waste, meat, and leather, as well as other raw materials (Mikulionok and Radchenko, 2012). Single-screw and twin-screw extruders are available for recycling processed materials. However, both have different process parameters. Single-screw and twin-screw extruders have some differences and benefits depending on the plastic being processed (Rosato and Knovel (Firm), 1998). In polymer processing technology, screw extrusion is the most important operation (Covas and Gaspar-Cunha, 2001).

Plastic extrusion is a process in which plastic/polymer material is melted and extruded through a die to create a desired shape. Most commonly, plastic extruded materials are formed into a cylindrical shape. To maintain the uniformity of extruded material, some arrangements are made to preheat the material (Al-Salem *et al.*, 2010). Cooling time and rolling speed of the material plays a major role in dimensional accuracy and properties of the wire being extruded (Wang *et al.*, 2011). Most of the plastic materials are available in the form of powder or granules. These are processed at room temperature. The plastic extrusion machine melts the material and homogenizes it before it enters the die. Conversion from a cold state to a hot state accounts for some energy. The surface profile depends on the cross-sectional shape, surface angle, and layer thickness (Ahn *et al.*, 2009). The ratio of the channel depth in the feed section to the channel depth in the metering section is often referred to as the compression ratio of the screw. Pumping action is basically forced flow of melted plastic from hopper end to die end. It is only effective if feeding volume is more than volume coming out from die front or die outlet. Because compression tries to decrease the volume. Further volume ratio and compression ratio both are same (Campbell and Spalding, 2013).

The extruder has the following parts:

- Hopper.
- Cylindrical barrel.
- Screw.
- Die head.
- Motor (for running of the screw).

The material enters the barrel through the hopper via gravity. The cylindrical barrel is surrounded by heaters that can be controlled manually with a set of specific temperature ranges. Generally, the temperature range of a normal screw extruder is up to 275°C, which is enough to melt thermoplastic materials. As material enters the barrel, the material starts heating up. The screw starts leading the material in the forward direction toward the die. The length of the barrel plays a major role. The role of screw speed is also important. If the screw has more speed, then the material will not melt properly, because the material will lead at a faster speed. If the speed of the screw is low, then the material will be overly melted and the wire will not form properly.

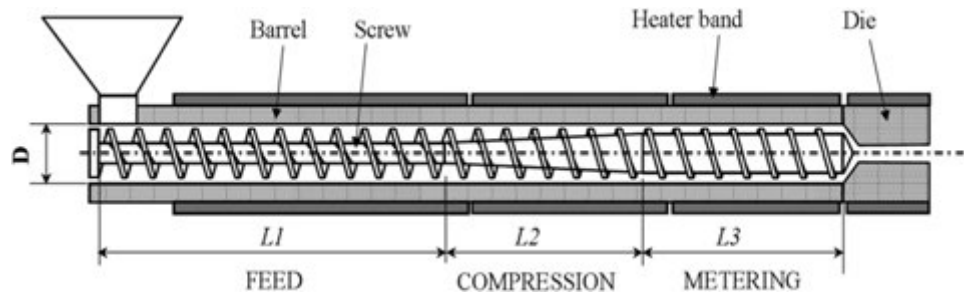


Fig. 1 Schematic of a single-screw extruder (Covas and Gaspar-Cunha, 2001).

The screw pushes the material into the barrel and leads it to the die. There can be multiple heating zones. Those heating zones gradually increase the temperature of the material. The pressure, which the screw is exerting on the material, may reach to 5000 psi (34 MPa). Then, material reaches the breaker plate, which creates back pressure. This is required for uniform mixing and uniform melting of material. After passing through the breaker plate, material arrives at the die, starts passing through it, and wire is formed. **Fig. 1** shows the basic schematic of single-screw extruder.

Screw extruders are capable of expelling material through a die under high pressure. The screw inside the barrel continuously exerts pressure on the material being processed inside. Some researchers have worked on reinforcements for different materials in polymer material. After processing the material in a single-screw extruder machine, wires are formed and then fed into the FDM commercial setup to make cylindrical pins.

FDM

One of the most common rapid prototyping (RP)/AM processes is FDM (Espalin *et al.*, 2014). Rapid prototypes can be of invaluable help in testing esthetic, functional, and engineering performance of a product during its development cycle. In principle, any physical model should reproduce all relevant product properties at an accuracy level consistent with the intended evaluation stage (Armillotta, 2006). Rapid manufacturing is one of the manufacturing technologies used for fabrication of three-dimensional (3D) models using the layered manufacturing (LM) process by stacking and bonding thin layers (Ahn *et al.*, 2009). LM processes are often used in various fields such as medical sciences, jewelry, construction industry, automobile industry, aircraft industry, and others (Chua *et al.*, 2003; Gebhardt and Gibson, 2003/2006; Venuvinod and Ma, 2004). Creative production techniques have the advantage of manufacturing products by AM without the need for forming tool (Bagsik and Schöppner, 2011). It is also important to highlight that the wrong choice of process parameters may result in a lack of adherence between layers and even to the platform, resulting in warping of the object and faulty formation of layers (Cunico, 2013).

As a consequence of the process characteristics, negative surfaces are generally produced by the deposition of a support material that is removed at the end of the manufacturing stage. This stage is called the postprocessing stage (Volpato, 2007; Gibson *et al.*, 2010). It is important to note that even though in some cases the support material is water-soluble, the cost of the material is extremely high, making the process more expensive (Cunico, 2013). Commercially available RP methods include the following: stereo-lithography, selective laser sintering, FDM, laminated object manufacturing, ballistic particle manufacturing, and 3D printing (Pham and Gault, 1998). Among these, FDM is the most preferred and simple method for RP. **Fig. 2** shows the schematic of the FDM process.

In FDM, a feed stock filament wire is used, and usually that wire comprises acrylonitrile butadiene styrene (ABS). ABS has some specific properties, such as tensile strength, Young's modulus, and percentage elongation. Many researchers have worked on parametric optimization of FDM with ABS as a filament (Panda, 2009). In this study, FDM from Stratasys USA was used. This machine can only run ABS wire with a melt flow index (MFI) of 2.41 g/10 min.

A pilot experimentation has been performed to find MFI values by selecting different proportions of SiC and Al₂O₃ in the Nylon-6 matrix.

Case Study of Polymer Single-Screw Extrusion

To study the effect of reinforcement particle size and to compare the properties of the obtained filament with single and hybrid reinforcements, two case studies are discussed here.

Case Study 1

In case study 1, an alternative FDM filament wire was fabricated through the extrusion process. For filament development, Al₂O₃ powder (supplied by Thomus Bakers) and Nylon-6 granules were used as reinforcement and polymer matrix, respectively. Three

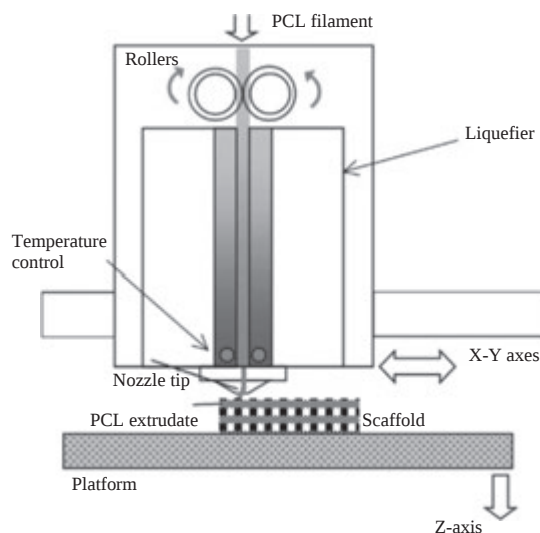


Fig. 2 Schematic of the FDM extrusion and deposition process (Zein *et al.*, 2002).

different sizes of Al_2O_3 powder (SPS, DPS, and TPS) were used to study the effect of the reinforcement particle size on desirable characteristics of filament and its resulting parts. Because the aim of the present study was to replace the commercial filament (ABSP-430) with an alternative prepared filament, to have a successful run in FDM, the rheological property of the alternative filament proportion was matched with ABSP-430 (2.41 g/10 min). MFI, one of the prominent rheological tests (Garg and Singh, 2015), was performed for various combinations of Nylon-6 and Al_2O_3 powder, as shown in Table 1. The test was performed using the melt flow index (pictorial view given in Fig. 3) as per the ASTM-D1238 standard (ie, at a temperature of 230°C and a force of 3.8 kg).

Although Table 1 indicates that none of the combinations obtained similar MFI values, the filament wires prepared could be used for open-source FDM systems. Therefore, some of the proportions were selected for filament development on a single-screw extruder at fixed processing parameters (mentioned in Table 2). Table 3 shows the various output parameters for this study.

Testing for mechanical properties

Table 4 summarizes the average of three runs for various mechanical properties (such as percentage elongation, tensile strength, yield strength, and Young's modulus) of selected compositions (as per Table 1) as tested on a universal tensile tester (UTM). The tensile properties of feed stock filament wires were tested as per the ASTM-638 standard. The mechanical properties tested are rate-dependent and were tested at strain rate of 50 mm/min.

Design Expert software was used to analyze the results for fabricated filaments. It offers comparative tests, screening, characterization, optimization, robust parameter design, mixture designs, and combined designs, and it provides test matrices for screening up to 50 factors. Statistical significance of these factors is established with analysis of variance (ANOVA). Graphical tools help to identify the impact of each factor on the desired outcomes and reveal abnormalities in the data. Based on Table 4, and by applying the mixture design (user-defined model with four components and four responses), ANOVA for the mixed quadratic model was performed (see Table 5).

The F-value of 8.47 implies that the model is significant. There is only a 1.41% chance that the F-value this large could occur due to noise. Values of Prob>F less than 0.0500 indicate that the model terms are significant. In this case, linear mixture components AC and BC are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), then model reduction may improve the model. The R-values along with mean and standard deviation values are provided in Table 6.

After excluding a one-outlier value from the model in Design Expert, various R-squared values were obtained (Table 7). The R-squared value is a statistical measure of how close the data are to the fitted regression line. It is also known as the coefficient of determination. According to Table 6, it was 0.9824, which is a satisfactory value and signifies that the developed statistical model yielded a good fit.

The adjusted R-squared value compares the explanatory power of regression models that contain different numbers of predictors. It increases only if the new term improves the model more than would be expected by chance. It decreases when a predictor improves the model by less than expected by chance. The adjusted R-squared can be negative, but it is usually not. It is always lower than the R-squared value. In the present study, in Table 6, it is 0.9718, which is less than the R-squared value.

The predicted R-squared value indicates how well a regression model predicts responses for new observations. If the predicted R-squared is much lower than the regular R-squared, then there is a chance that the model contains too many terms. In the present study (as per Table 6), it is 0.9381, which is in reasonable agreement with the adjusted R-squared value.

Table 1 Results of MFI Al₂O₃-reinforced Nylon-6

<i>S. no.</i>	<i>Nylon-6</i>	<i>Al₂O₃ (150 μm)</i>	<i>Al₂O₃ (120 μm)</i>	<i>Al₂O₃ (100 μm)</i>	<i>MFI (g/10 min)</i>
SPS	50	0	0	50	14.22
	50	0	50	0	5.23
	50	50	0	0	8.9
	60	0	0	40	15.96
	60	0	40	0	6.61
	60	40	0	0	7.8
DPS	50	0	5	45	8.92
	50	0	10	40	8.54
	50	0	15	35	6.25
	50	0	20	30	4.92
	50	0	25	25	3.25
	50	0	30	20	5.55
	50	0	35	15	6.11
	50	0	40	10	5.25
	50	0	45	5	10.15
	60	0	5	35	11.98
	60	0	10	30	10.54
	60	0	15	25	5.96
	60	0	20	20	5.82
	60	0	25	15	8.25
	60	0	30	10	8.35
	60	0	35	5	15.55
DPS	50	5	45	0	16.45
	50	10	40	0	12.25
	50	15	35	0	12.35
	50	20	30	0	7.58
	50	25	25	0	4.29
	50	30	20	0	10.29
	50	35	15	0	12.84
	50	40	10	0	13.84
	50	45	5	0	18.52
	60	5	35	0	18.25
	60	10	30	0	14.28
	60	15	25	0	9.85
	60	20	20	0	4.72
	60	25	15	0	4.95
	60	30	10	0	8.45
	60	35	5	0	9.24
DPS	50	5	0	45	8.12
	50	10	0	40	6.35
	50	15	0	35	3.45
	50	20	0	30	2.98
	50	25	0	25	2.82
	50	30	0	20	3.25
	50	35	0	15	5.29
	50	40	0	10	5.84
	50	45	0	5	9.8
	60	5	0	35	9.25
	60	10	0	30	8.36
	60	15	0	25	4.92
	60	20	0	20	4.15
	60	25	0	15	8.54
	60	30	0	10	10.59
	60	35	0	5	12.25
TPS	50	5	5	40	24.45
	50	5	10	35	22.24
	50	5	15	30	16.58
	50	5	20	25	15.58
	50	5	25	20	17.49
	50	5	30	15	10.26
	50	5	35	10	9.48

Table 1 Continued

<i>S. no.</i>	<i>Nylon-6</i>	<i>Al₂O₃ (150 μm)</i>	<i>Al₂O₃ (120 μm)</i>	<i>Al₂O₃ (100 μm)</i>	<i>MFI (g/10 min)</i>
50	5	5	40	5	7.54
50	40	40	5	5	14.55
50	35	35	5	10	9.59
50	30	30	5	15	10.55
50	25	25	5	20	12.55
50	20	20	5	25	14.87
50	16.66	16.66	16.67	16.67	4.12
50	15	15	5	30	12.54
50	10	10	5	35	14.59
50	35	35	10	5	5.48
50	30	30	15	5	6.52
50	25	25	20	5	8.54
50	20	20	25	5	9.64
50	15	15	30	5	10.55
50	10	10	35	5	10.54
60	5	5	5	30	28.12
60	5	5	10	25	25.56
60	5	5	15	20	17.55
60	5	5	20	15	15.86
60	5	5	25	10	18.12
60	5	5	30	5	12.59
60	30	30	5	5	19.48
60	25	25	5	10	14.37
60	20	20	5	15	15.91
60	15	15	5	20	16.49
60	10	10	5	25	18.88
60	13.34	13.34	13.33	13.33	4.80
60	5	5	5	30	14.54
60	25	25	10	5	8.29
60	20	20	15	5	9.55
60	15	15	20	5	11.59
60	10	10	25	5	11.73
60	5	5	30	5	14.59

Note: SPS represents single particle size (of 100 μm), DPS represents two particle sizes in equal proportion by weight (of 100 μm and 120 μm), and TPS represents three particle sizes in equal proportion by weight (of 100 μm, 120 μm, and 150 μm).

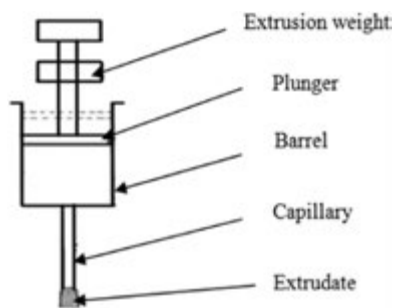


Fig. 3 Schematic of MFI tester.

Table 2 Input parameters of single-screw extruder

<i>S. no.</i>	<i>Die temperature (°C)</i>	<i>Barrel temperature (°C)</i>	<i>Screw speed (rpm)</i>	<i>Take-up speed (rpm)</i>
1	180	200	15	20

Table 3 List of output parameters

Parameters	Elongation	Tensile strength	Yield strength	Young's modulus	Wear
Units	%	kg/mm ²	kg/mm ²	kg/mm ²	μm

Table 4 Mechanical properties of different prepared filament wires (average values of three repetitions)

S. no.	Nylon-6	Al ₂ O ₃ 150 μm	Al ₂ O ₃ 120 μm	Al ₂ O ₃ 100 μm	MFI	% Elongation	Tensile strength ^a	Yield strength ^a	Young's modulus ^a
SPS	50	0	50	0	5.23	5.23	2.68	0.33	69.82
	60	0	40	0	6.61	6.61	3.99	0.96	55.10
DPS	50	25	25	0	4.29	4.29	3.25	0.74	88.90
	60	20	20	0	4.72	4.72	3.38	0.31	70.22
	50	25	0	25	2.82	2.82	2.63	1.65	47.12
	60	20	0	20	4.15	4.15	3.71	0.99	36.70
	50	0	25	25	3.25	3.25	4.54	1.14	28.10
	60	0	20	20	5.82	5.82	4.51	3.18	21.68
TPS	50	16.66	16.67	16.67	4.12	4.12	3.12	1.82	55.71
	60	13.34	13.33	13.33	4.80	4.80	2.35	1.78	43.14
Pure (Nylon-6)	–	–	–	–	10.61 ^b	5.23	5.23	–	112–1630
ABS (P-430)	–	–	–	–	2.41	3	3.77	–	232

^aPresented in kg/mm².^bSource: Singh and Singh (2016).**Table 5** ANOVA for mixture quadratic model (partial sum of squares)

Source	Sum of squares	DF	Mean square	F value	Prob>F
Model	167.55	3	55.85	8.47	0.0141
Linear mixture	167.55	3	55.85	8.47	0.0141
Residual	39.56	6	6.59		
Corollary total	207.11	9			

Table 6 Statistical analysis

SD	0.79
Mean	8.77
R-squared	0.9824
Adjusted R-squared	0.9718
Predicted R-squared	0.9381
Adequate precision	24.910

Table 7 Standard error for components

Component	Coefficient estimate	DF	Standard error	95% CI, low	95% CI, high
Nylon-6	–14.30	1	7.35	–32.29	3.69
Al ₂ O ₃ 150 μm	1.73	1	3.32	–6.38	9.85
Al ₂ O ₃ 120 μm	16.21	1	1.87	11.62	20.79
Al ₂ O ₃ 100 μm	9.88	1	3.33	1.72	18.03

Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. A ratio of 24.910 indicates an adequate signal. This model can be used to navigate the design space. The values of different model components and the values of their standard errors are listed in [Table 7](#).

After analyzing the results for various mechanical properties, a linear model was developed to predict the earliest outputs. [Eq. 1](#) shows the model for percentage elongation of the filament wire:

$$\text{Percentage elongation} = | -14.29722 \times a + 17.76623 \times b + 46.71259 \times c + 34.04853 \times d | \quad (1)$$

Where, a, b, c, and d represent %wt of Nylon-6, Al_2O_3 (150 μm), Al_2O_3 (120 μm), and Al_2O_3 (100 μm), respectively.

To validate and check the adequacy of the model, a corollary was performed as per the experiment 10 in [Table 4](#). [Eq. \(2\)](#) shows the predicted value of percentage elongation:

$$\begin{aligned} \text{Percentage elongation} &= | -14.29722 \times 0.6 + 17.76623 \times 0.1334 + 46.71259 \times 0.1333 + 34.04853 \times (0.1333) | \\ &= 4.55(\text{predicted value}) \end{aligned} \quad (2)$$

The predicted value was compared with the experimental value, and it was found that the percentage of error is less than 3%; therefore, it can be concluded that the model developed is adequate to predict the response in terms of percentage elongation.

Similarly, the mathematical model for tensile strength was developed and provided [Eq. \(3\)](#).

$$\text{Tensile strength} = | 0.60983 \times a + 8.24141 \times b + 5.33765 \times c + 1.95317 \times d | \quad (3)$$

To validate the model, a corollary was performed in a similar way (see [Eq. \(4\)](#)).

$$\begin{aligned} \text{Tensile strength} &= | 0.60983 \times 0.6 + 8.24141 \times 0.1334 + 5.33765 \times 0.1333 + 1.95317 \times 0.1333 | \\ &= 2.24(\text{predicted value}) \end{aligned} \quad (4)$$

The predicted value was compared with the experimental value. The percentage error was checked and was less than 4%.

Further, a mathematical model for yield strength was developed (see [Eq. \(5\)](#)) and validated by performing a corollary (provided in [Eq. \(6\)](#)).

$$\text{Yield strength} = | 2.66776 \times a - 0.74963 \times b - 1.41875 \times c + 2.78802 \times d | \quad (5)$$

Similarly, [Eq. \(6\)](#) shows results for the corollary that was performed.

$$\begin{aligned} \text{Yield strength} &= | 2.66776(0.6) - 0.74963(0.1334) - 1.41875(0.1333) + 2.78802(0.1333) | \\ &= 1.55 \text{ (predicted)} \end{aligned} \quad (6)$$

After performing the corollary, the percentage error was found to have very low predicted and experimental values.

Similarly, a mathematical model for Young's modulus was developed (see [Eq. \(7\)](#)).

$$\text{Young's modulus} = | -4.44512 \times a + 220.15468 \times b + 144.26259 \times c - 22.85559 \times d | \quad (7)$$

After obtaining the mathematical model, it was cross-checked for validation. [Eq. \(8\)](#) shows the corollary performed to validate that model.

$$\begin{aligned} \text{Young's modulus} &= | -4.44512 \times 0.6 + 220.15468 \times 0.1334 + 144.26259 \times 0.1333 - 22.85559 \times 0.1333 | \\ &= 42.88 \text{ (predicted)} \end{aligned} \quad (8)$$

After performing the corollary, the percentage error was found to be less than 0.67%.

Wear testing

After testing sample wires on a UTM, filament wire was prepared on a screw extruder by using the same compositions that were selected previously. Then, those wires were made to run on the FDM machine, and pins of specific dimensions (as per ASTM standard) were made to test the wear of the material using a pin-on-disk machine. [Fig. 4](#) shows the pins prepared by the FDM machine.

Friction loss plays a major role in the performance and reliability of components such as plastic deformation, adhesion, wear, fracture, and fatigue, which make excessive wear a critical parameter. Testing is often used to predict friction and wear characteristics of materials that need closer investigation ([Bortoleto et al., 2013](#)). Polymers and elastomers in sliding contacts often operate in a certain set of conditions called "thermal control regime," in which the contact temperature affects the friction and wear. Adhesive wear mechanisms always occur in sliding contacts ([Lisowski and Stolarski, 1981](#)). Friction causes the asperities on one surface to become cold-welded to the other surface. The volume of material transferred for adhesive wear is proportional to the real area of contact and the sliding distance ([Archard, 1953](#)). The tribological measurement is a lengthy and expensive process ([Novak and Polcar, 2014](#)); therefore, the number of experiments should be optimum. First, the wire made of particular material from the extruder is formed, and then the wire is made to run in the FDM machine. Then, pins of a specific dimension according to ASTM standards are formed with the FDM machine. These pins are used for pin-on-disk. This machine contains a holder to hold



Fig. 4 Pin prepared by the FDM machine.

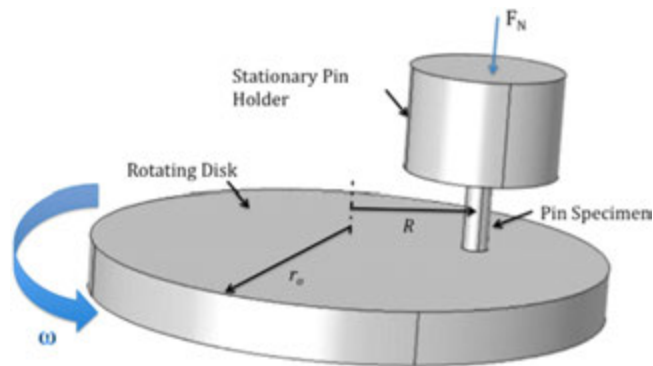


Fig. 5 Schematic of the pin-on-disk process (Kennedy *et al.*, 2015).

the pin and an E-31 disk (Ducom machine setup) on which pin is rubbed. Different sizes of holders are available. **Fig. 5** shows a schematic of the pin-on-disk process.

The disk is rotated by the motor and controlled by a manual control box provided with the machine. A weight holder is attached with a single link mechanism. As weight is put on, it exerts pressure on the holder; therefore, the pin is pressed on the disk and then the machine is set to run for a particular time (Singh, 2015). In the present study, Nylon-6 pins reinforced with different metallic fillers were used and showed much less wear compared to ABS pins. Many researchers have reported that polymers and polymer composites, when sliding against a steel counterface, have less wear due to the formation of a thin protective film (Nagaraju *et al.*, 2011). To achieve proper rubbing of the pins, the counter sliding surface for the pins was prepared by gluing emery paper (600 grit size) on a steel disk (EN-32; Hardness 65 HRC). After starting the machine, the disk starts rotating and pins start rubbing on it. Hence, the wear phenomenon begins. This machine is attached to wear and weight sensors that further send signals to the software installed on the computer system provided with the machine. Then, the software monitors the signal and graphs are formed accordingly.

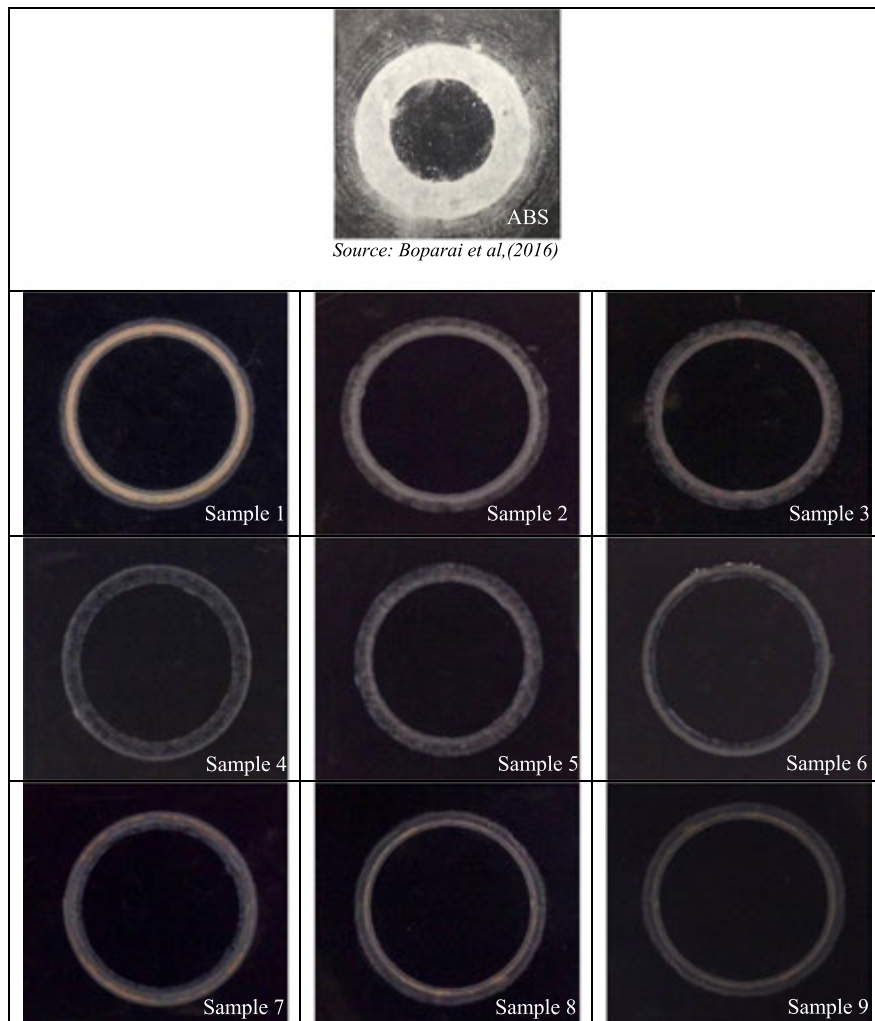
The wear test was performed as per the ASTM G 99 standard under dry sliding conditions at room temperature with a sliding speed of 190 rpm, 80-mm track diameter, and 5-N load for a 10-min test run. The wear value for a standard ABS is 409 μm under the same boundary conditions used for this research work. The machine was equipped with a data acquisition system. In this study, pins were made of polymer material; therefore, the rubbing of pins on the metallic disk showed negligible wear. **Table 8** summarizes the values obtained after wear testing.

It can be clearly seen that values of Nylon-6 pins are very low compared to wear values of ABS. This may be due to the presence of metallic parts in Nylon-6, because metallic parts have high wear resistance as compared to plastic materials. After experimentation with pin-on-disk, wear track was obtained from the emery papers that were glued on the disk of the machine. **Fig. 6** illustrates the comparison of ABS wear behavior and prepared pins.

In **Fig. 6**, the wear track for ABS clearly shows the extent of wear on pins when rubbed against the disk. The amount of wear for ABS was much more than that for other prepared pins. Tracks for composite material-based pins are quite sharper than for tracks of the ABS pins. Volume loss of material generally caused by abrasion and adhesion phenomena normally starts with abrasion (Nagaraju *et al.*, 2011). To understand the wear phenomenon, SEM analysis was performed to ensure the presence of every type of particle used in the different proportions. **Fig. 7** shows SEM images of composite pins.

Table 8 Results of wear tests

Sample	Type of reinforcement	Nylon-6	Al_2O_3 150 μm	Al_2O_3 120 μm	Al_2O_3 100 μm	Wear (in μm)
1	SPS	50	0	50	0	161
2		60	0	40	0	140
3		50	25	25	0	138
4	DPS	60	20	20	0	101
5		50	25	0	25	119
6		60	20	0	20	106
7	TPS	50	0	25	25	142
8		60	0	20	20	145
9		50	16.66	16.67	16.67	134
10		60	13.34	13.33	13.33	118


Fig. 6 Wear track for ABS and Nylon-6 pins.

In Fig. 7, it is clearly visible that the extent of wear on developed pins is low compared to ABS pins due to the presence of abrasive particles. The presence of particles has been proven by SEM analysis (see Fig. 7).

SEM analysis of every pin was performed, which ensures the uniform presence of every type of particle used in the subsequent mixture, thereby ensuring cohesion between the printed layers. After finding the wear for the composite material, Design Expert software was used to model the wear results for the different pins. The mixture module using response surface methodology was used to model the results. This mathematical tool helps to create a mathematical model for wear results of different compositions. Tables 8 and 9 show ANOVA results for wear data.

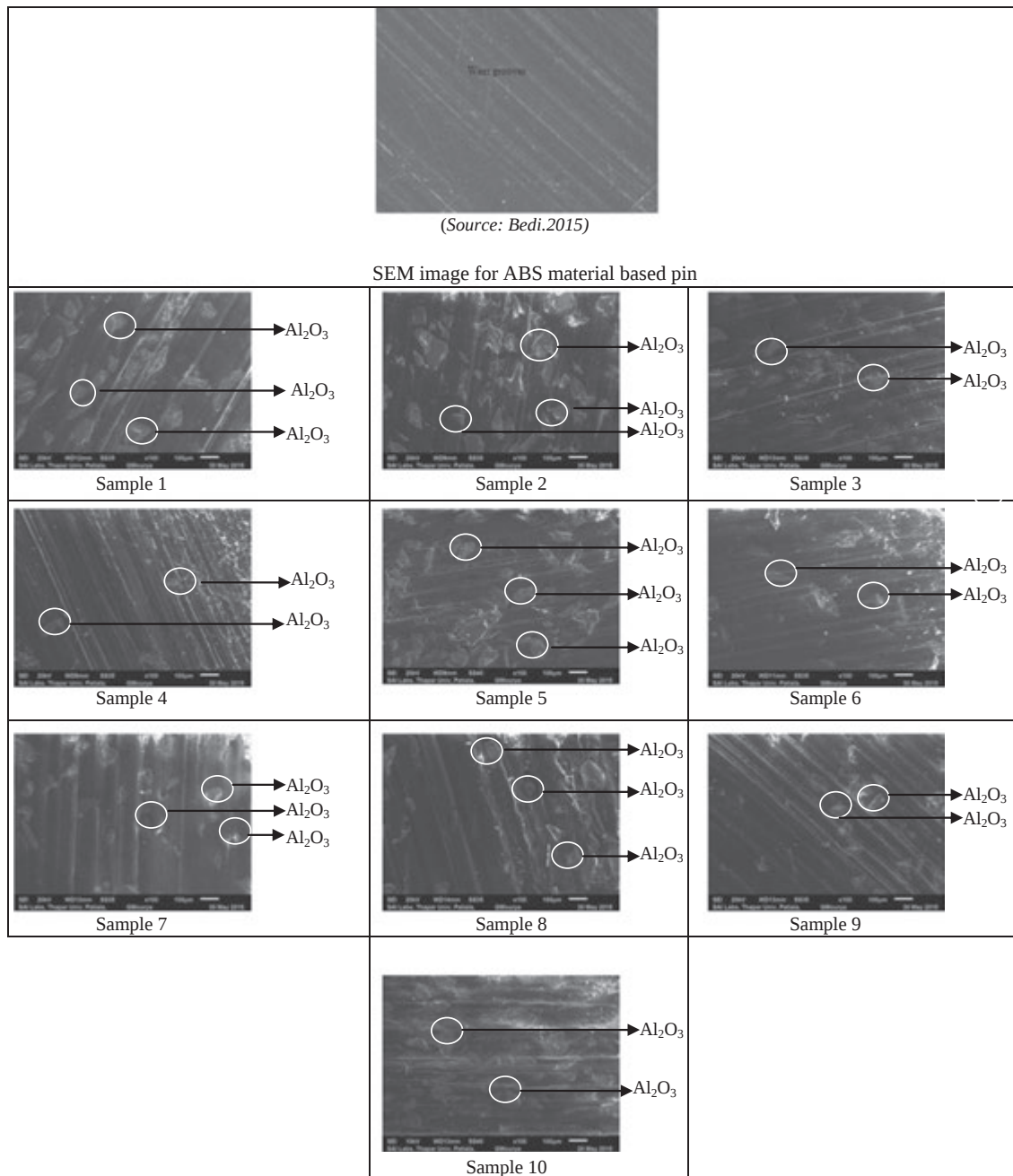


Fig. 7 SEM results of different pin samples.

The F-value of 10.55 implies that the model is significant. There is only a 0.83% chance that an F-value this large could occur due to noise. Values of Prob>F less than 0.0500 indicate that the model terms are significant. In this case, linear mixture components AC and BC are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), then model reduction may improve the model. The R-values along with the means and standard deviations are provided here:

SD:	9.21
Mean:	130.40
R-squared:	0.8406
Adjusted R-squared:	0.7609
Predicted R-squared:	0.4791
Adequate R-squared:	9.450

Table 9 ANOVA for mixture linear model with standard error values

<i>Source</i>	<i>Sum of squares</i>	<i>DF</i>	<i>Mean square</i>	<i>F</i>	<i>Prob>F</i>
Model	2681.78	3	893.93	10.55	0.0083
Linear mixture	2681.78	3	893.93	10.55	0.0083
Residual	508.62	6	84.77		
Corollary total	3190.40	9			
<i>Standard error for components</i>					
<i>Component</i>	<i>Coefficient estimate</i>	<i>DF</i>	<i>Standard error</i>	<i>95% CI, low</i>	<i>95% CI, high</i>
Nylon-6	54.13	1	26.37	– 10.38	118.65
Al ₂ O ₃ 150 μm	95.33	1	11.89	66.25	124.42
Al ₂ O ₃ 120 μm	161.23	1	6.72	144.79	177.67
Al ₂ O ₃ 100 μm	143.11	1	11.95	113.87	172.35

Adequate precision measures the signal-to-noise ratio. A ratio more than 4 is desirable. The ratio of 9.450 indicates an adequate signal. This model can be used to navigate the design space.

After complete analysis by Design Expert, the following mathematical model for wear in terms of actual components was obtained (see Eq. (9)).

$$\text{Wear} = |54.13300 \times a + 136.53552 \times b + 268.33180 \times c + 232.08541 \times d| \quad (9)$$

After obtaining a mathematical model for wear, a corollary was performed in a similar way to check validity of the obtained model. Eq. (10) shows the corollary for the wear model.

$$\text{wear} = |54.13300 \times 0.6 + 136.53552 \times 0.1334 + 268.33180 \times 0.1333 + 232.08541 \times 0.1333| = 117 \text{ (predicted)} \quad (10)$$

The percentage error was below 0.8%.

Case Study 2

In the second case study, an alternative FDM filament wire was fabricated in a similar way; however, in this case study SiC and Al_2O_3 were used as reinforcements in the Nylon-6 polymer matrix. For establishing MFI, a similar number of runs were performed as shown in Table 10.

Based on Table 10, it was decided to perform the final experimentation with 125- μm SiC and Al_2O_3 because with this size of reinforcement, the MFI value is close to the MFI of commercially available ABS material (ie, 2.4 g/10 min; see S. no. 10–12, 14–18, and 20). After establishing the MFI, further experimentation was performed to observe the values for different properties. The variable input parameter in this study is only composition/proportion of reinforcement. The proportions of SiC (125 μm) and Al_2O_3 (125 μm) were varied. The spools of filament wire were prepared with a single-screw extruder, installed on an FDM machine, and checked for usability. The fixed input parameters for single-screw extruders were kept the same as shown in Table 2.

After preparation of wire, mechanical tests were performed; data obtained from those tests are shown in Table 11.

Table 11 describes the various values of MFI, peak load, yield strength, Young's modulus, and percentage elongation. Better values of different properties were obtained for some combinations. Further analysis of results is discussed in the Results section.

After inputting the data in Design Expert software (based on Table 11) and by applying Mixture Design (user-defined model with three components and four responses), the prepared model was analyzed and mathematical models were obtained and counter-verified with various derived values from actual experimentation. Table 12 shows ANOVA for the mixture quadratic model.

The F-value of 24.53 implies that the model is significant. The values of Prob>F less than 0.0500 indicate that the model terms are significant. In this case, linear mixture components ab and ac are significant model terms. Values more than 0.1000 indicate that the model terms are not significant. If there are many insignificant model terms (not counting those required to support

Table 10 Observations of pilot experimentation for MFI^a

S. no.	Nylon-6 (a)	SiC (b)			Al ₂ O ₃ (c)			MFI (g/10 min)
		Grain size			Grain size			
		149 μm	125 μm	106 μm	149 μm	125 μm	106 μm	
1	50	25	–	–	–	25	–	4.078
2	50	–	–	25	–	25	–	4.0775
3	50	25	–	–	25	–	–	4.33
4	60	20	–	–	20	–	–	8.97
5	55	11.25	11.25	–	11.25	11.25	–	7.08
6	65	8.75	8.75	–	8.75	8.75	–	7.42
7	70	5	5	5	5	5	5	4.88
8	75	4.17	4.17	4.17	4.17	4.17	4.17	6.54
9	50	–	5	–	–	45	–	1.55
10	50	–	10	–	–	40	–	2.42
11	50	–	20	–	–	30	–	2.72
12	50	–	30	–	–	20	–	2.9
13	40	–	30	–	–	30	–	1.14
14	45	–	25	–	–	30	–	1.84
15	45	–	30	–	–	25	–	2.36
16	50	–	25	–	–	25	–	2.76
17	55	–	25	–	–	20	–	3.149
18	60	–	20	–	–	20	–	4.613
19	70	–	15	–	–	15	–	7.501
20	50	–	15	–	–	35	–	2.6

^aSource: Singh (2015).

Table 11 Mechanical properties of different filament wires

S. no.	a	b	c	MFI (g/10 min)	Peak load (kgf)	Peak load (kg/mm ²)	Young's modulus (kg/mm ²)	Percentage elongation (%)
1	50	10	40	2.42	12.15	2.9	66.55	10.40
2	50	20	30	2.72	7.85	1.57	31.17	9.35
3	50	25	25	2.76	14.25	1.3	55.49	6.75
4	50	30	20	2.9	8.35	1.2	48.83	6.23
5	45	25	30	1.84	8.20	2.3	167.14	1.55
6	45	30	25	2.36	12.15	1.22	47.28	8.83
7	55	25	20	3.15	8.30	0.48	53.57	5.20
8	60	20	20	4.613	12.60	3.53	46.86	8.83
9	50	15	35	2.6	8.95	3.91	54.89	9.77

Note: Here a, b, and c represent Nylon-6, SiC (125 μm), and Al_2O_3 (125 μm), respectively.

hierarchy), then model reduction may improve the model. R-values along with means and standard deviations are provided in Table 13.

In Table 13, adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. A ratio of 14.740 indicates an adequate signal. This model can be used to navigate the design space. After complete analysis by Design Expert, an equation for percentage elongation in terms of the actual component was obtained.

Model Validation

To validate the model, a corollary was performed with a defined set of input parameters, where total proportion weight was 1. In all the corollaries, a random set of values for a, b, and c were used. Then, the prepared models were discussed and cross-checked to verify the authenticity of empirical realtions/mathematical model.

After analyzing the results for various mechanical properties, a model was developed to predict the earliest outputs, with a, b, and c representing Nylon-6, SiC, and Al_2O_3 . To validate each mathamatical model, cross-checking was performed with a certain set of defined values given in Table 14.

After analyzing the results for various mechanical properties, a model was developed to predict the earliest outputs. Eq. (11) shows the model for the MFI percentage of the filament wire:

Eq. (11) shows the model for the MFI of filament wire

$$\text{MFI} = | -0.16157 \times a + 30.47414 \times b - 57.48014 \times c - 48.77143 \times a \times b + 123.57143 \times a \times c + 4.57143 \times b \times c | \quad (11)$$

To validate and check the adequacy of the model, a corollary was performed as shown in Table 14. Eq. (11) shows the corollary for MFI.

$$\begin{aligned} \text{MFI} = | & -0.16157 \times 0.50 + 30.47414 \times 0.1 - 57.48014 \times 0.4 - 48.77143 \times 0.50 \times 0.1 + 123.57143 \times 0.50 \times 0.4 \\ & + 4.57143 \times 0.1 \times 0.4 | = 2.43(\text{predictedvalue}) \end{aligned} \quad (12)$$

After obtaining the predicted value, the percentage error was very negligible (1.43%). Therefore, the model was found to be satisfactory.

In a similar way, the mathematical model for percentage (%) elongation has been developed and validated. Eq. (13) shows the model for percentage elongation.

$$\begin{aligned} \% \text{ Elongation} = | & + 58.23400 \times a + 849.01400 \times b - 861.86600 \times c - 1826.8000 \times a \times b \\ & + 1651.60000 \times a \times c + 56.00000 \times B \times c | \end{aligned} \quad (13)$$

The model developed in Eq. (13) was validated by performing a corollary given in Eq. (14).

$$\begin{aligned} \% \text{ Elongation} = | & + 58.23400 \times 0.50 + 849.01400 \times 0.1 - 861.86600 \times 0.4 - 1826.80000 \times 0.5 \times 0.1 \\ & + 1651.60000 \times 0.5 \times 0.4 + 56.00000 \times 0.1 \times 0.4 | = 10.4944 \text{ (predicted value)} \end{aligned} \quad (14)$$

The percentage error of the predicted value of this corollary is less than 0.09%. Therefore, the model is satisfied.

A mathematical model for Young's modulus was developed. Eq. (15) shows the model developed for Young's modulus.

$$\begin{aligned} \text{Young's modulus} = | & - 111.400 \times a - 10918.76 \times b + 13945.5 \times c + 22768.8 \times a \times b - 27158.00000 \times a \times c \\ & - 1758.00000 \times b \times c | \end{aligned} \quad (15)$$

A corollary has been performed in a similar manner to validate the model developed in Eq. (16).

$$\begin{aligned} \text{Young's modulus} = | & - 111.400 \times 0.50 - 10918.76000 \times 0.10 + 13945.50000 \times 0.40 + 22768.80000 \times 0.50 \times 0.10 \\ & - 27158.00000 \times 0.50 \times 0.40 - 1758.00000 \times 0.10 \times 0.40 | = 67.144 \end{aligned} \quad (16)$$

Table 12 ANOVA for mixture quadratic model with standard error values

<i>Source</i>	<i>Sum of squares</i>	<i>DF</i>	<i>Mean square</i>	<i>F</i>	<i>Prob>F</i>
Model	60.18	5	12.04	24.53	0.0396
Linear mixture	30.74	2	15.37	31.32	0.0309
Residual	0.98	2	0.49		
Corollary total	61.16	7			
<i>Standard error for components</i>					
<i>Component</i>	<i>Coefficient estimate</i>	<i>DF</i>	<i>Standard error</i>	<i>95% CI, low</i>	<i>95% CI, high</i>
a-a	57.76	1	14.66	− 5.33	120.85
b-b	15.83	1	1.61	8.90	22.76
c-c	− 21.97	1	4.16	− 39.87	− 4.07
ab	− 114.18	1	25.81	− 225.21	− 3.14
Ac	103.22	1	16.35	32.88	173.57
bc	3.50	1	4.68	− 16.14	23.64

Table 13 R-values with means and standard deviation

S. no.	SD	Mean	R-squared	Adjusted R-squared	Predicted R-squared	Adequate R-squared
1	0.70	7.26	0.9840	0.9438	N/A	14.740

Table 14 Fixed values for model validation

S. no.	a	b	c
1.	0.50	0.10	0.40

After comparison of the predicted value of Young's modulus with the actual experimental value, the percentage error was less than 1.3%; therefore, the model is adequate.

Regarding mechanical properties, a mathematical model for yield strength was finally developed and is shown in Eq. (17).

$$\text{Yield strength} = |-3.52059 \times a + 1.07217 \times b + 11.28730 \times c| \quad (17)$$

Therefore, the model was cross-checked with a corollary for validation. Eq. (18) shows the corollary for yield strength.

$$\text{Yield strength} = |-3.52059 \times 0.5 + 1.07217 \times 0.10 + 11.28730 \times 0.40| = 2.86 \quad (18)$$

These equations were solved, and it can be seen that the results of the mathematical models are quite close to the actual values. Here, the percentage error is less than 1.3%, so these results could be termed significant. Furthermore, these equations are helpful for finding compositions based on tailor-made properties just by filling the desired values.

Wear Testing

Similarly, cylindrical pins were prepared using the FDM machine and tested for wear behavior. Table 15 shows the values obtained from wear testing various pins.

After obtaining values for wear testing, the values of the wear track were obtained in a manner similar to that of a previous case study. Fig. 8 show the wear tracks for various pins.

After wear testing, SEM analysis (see Fig. 9) was performed to ensure the presence of abrasive/metallic particles in Nylon-6.

After calculating the wear for the composite material, Design Expert software was used to model the wear results for the different pins. The mixture module of the response surface methodology tool was used to model the results. This mathematical tool helps to develop a mathematical model for different results of different compositions. The values of wear, as per Table 15, were input in this tool and analyzed. Table 16 shows ANOVA for the mixture quadratic model.

The F-value of 333.22 implies that the model is significant. There is only a 0.30% chance that a model F-value this large could occur due to noise. Values of Prob>F less than 0.0500 indicate that the model terms are significant. In this case, linear mixture components AC and BC are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), then model reduction may improve the model. The R-values along with means and standard deviations are provided in Table 17.

Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 47.743 indicates an adequate signal. This model can be used to navigate the design space. The values of different model components and the values of their standard errors are listed in Table 18.

After complete analysis by Design Expert software, the following equations in terms of actual components are as follows.

Wear test performance data of pins were placed into the software and the mathematical model was obtained (see Eq. (19)).

$$\text{Wear} = |-6338.60000 \times a + 653.40000 \times b - 24238.60000 \times c + 6000.00000 \times a \times b + 58960.00000 \times a \times c + 18400.00000 \times b \times c| \quad (19)$$

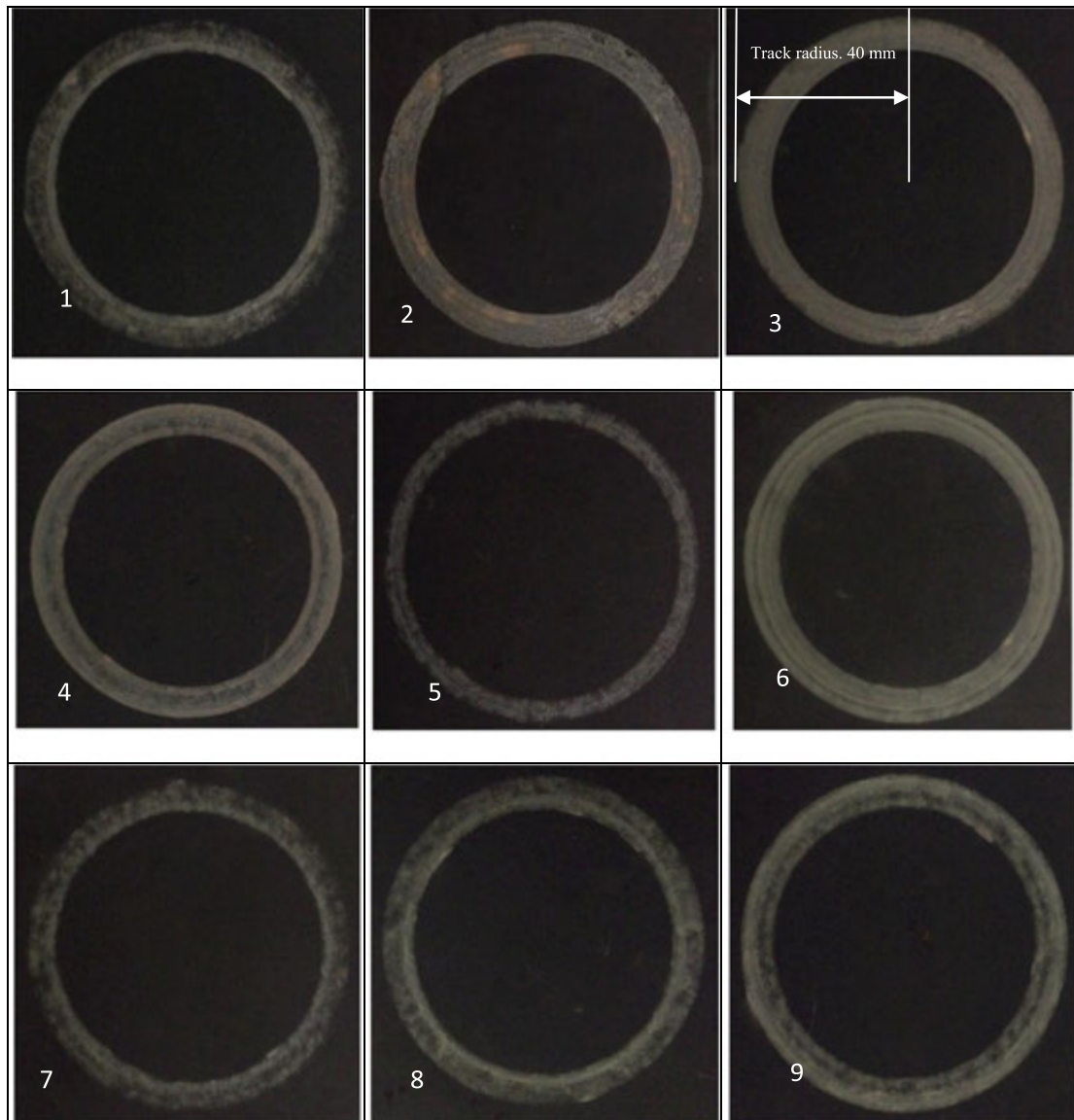
After development of the wear model, the feasibility of this model was counter-checked by performing a corollary. Eq. (20) shows the equation of the corollary performed.

$$\text{Wear} = |-6338.60000 \times .50 + 653.40000 \times .10 - 24238.60000 \times .40 + 6000.0000 \times .50 \times .10 + 58960.00000 \times .5 \times .40 + 18400.00000 \times .10 \times .40| = 28 \mu\text{m (predicted)} \quad (20)$$

Table 15 Results of wear tests

<i>S. no.</i>	<i>Nylon-6, a</i>	<i>SiC 125 μm, b</i>	<i>Al₂O₃ 125 μm, c</i>	<i>Wear (μm)</i>
1	50	10	40	28
2	50	20	30	242
3	50	25	25	199
4	50	30	20	81
5	45	25	30	54
6	45	30	25	107
7	55	25	20	60
8	60	20	20	51
9	50	15	35	50
10	^a ABS	0	0	409

^aBased on observations made by Boparai *et al.* (2016).

**Fig. 8** Wear track for composite pins.

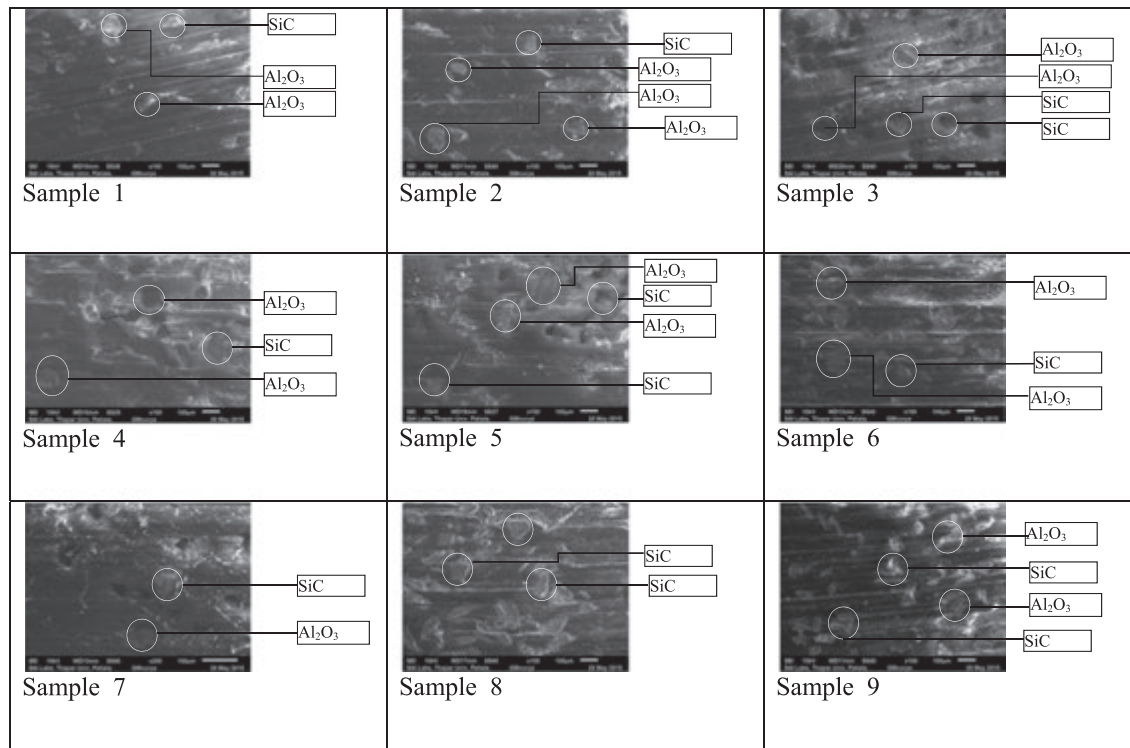


Fig. 9 SEM images.

Table 16 ANOVA for mixture quadratic model (partial sum of squares)

Source	Sum of squares	DF	Mean square	F	Prob > F
Model	42,652.30	5	8530.46	333.22	0.0030
Linear mixture	– 12,007.67	2	– 6003.83	– 234.52	1.0000
ab	103.62	1	103.62	4.05	0.1819
ac	24,932.35	1	24,932.35	973.92	0.0010
bc	29,624.00	1	29,624.00	1157.19	0.0009
Residual	51.20	2	25.60		
Corollary total	42,703.50	7			

Table 17 Statistical analysis for the wear model

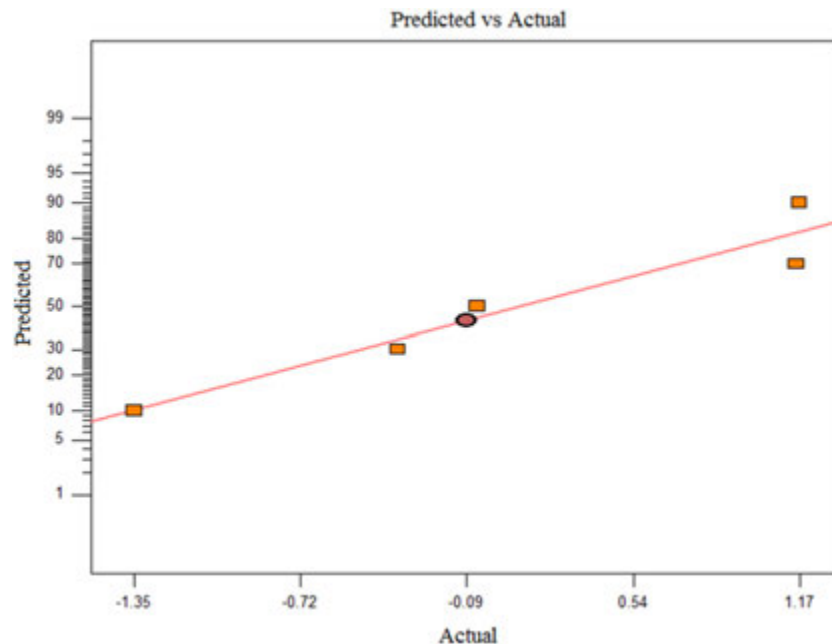
SD	5.06
Mean	118.75
C.V.	4.26
PRESS	N/A
R-squared	0.9988
Adjusted R-squared	0.9958
Predicted R-squared	N/A
Adequate precision	47.743

The percentage error was less than 2.14% after comparison of the predicted and experimental values; therefore, the model was adequate.

Fig. 10 shows the comparison between the actual and predicted values of wear. An actual value is obtained from experimentation and a predicted value is suggested by the software package. Hence, it can be clearly seen that predicted values are very close to the actual values obtained from the real experimentation. Similarly, graphs were also obtained and satisfactory results were found.

Table 18 Standard error for components

Component	Coefficient estimate	DF	Standard error	95% CI, low	95% CI, high
a-a	-177.00	1	105.91	-632.68	278.68
b-b	68.00	1	11.63	17.95	118.05
c-c	-657.00	1	30.06	-786.32	-527.68
ab	375.00	1	186.39	-426.99	1176.99
ac	3685.00	1	118.08	3176.94	4193.06
bc	1150.00	1	33.81	1004.54	1295.46

**Fig. 10** Actual and predicted values of wear.

After performing both case studies, better results were obtained in terms of mechanical and wear properties. However, in the first case study, the MFI values obtained were insufficient. However, further work was performed regarding formation of filament wire by selecting appropriate values to check and analyze results for different properties.

In the second case, very good results were obtained in terms of MFI, mechanical properties, and wear properties of filament wire and pins, respectively. Wear properties obtained in both case studies were very promising.

Conclusions

The outcomes of the present work show the feasibility of developing FDM wire from alternative materials with the single-screw extrusion process. Because ABS wire has limited mechanical and wear properties, alternative materials with tailor-made properties can be used. In this case, a wire comprising alternative material has been successfully developed and pins were successfully prepared. The values for wear and MFI have been established. A Nylon-6-based feed stock filament was successfully developed with hybrid reinforcement of SiC and Al₂O₃ of different sizes. The prototype/pins comprising composite materials have been developed with high resistance to wear. The wear track obtained in this study shows that the material is highly wear-resistant. The wear model was developed and cross-checked for accuracy. The wire used as feed stock filament for FDM with tailor-made wear properties can be easily predicted by the proposed empirical model.

Acknowledgment

The authors are thankful to the Institute of Engineering (GOI), Kolkata, and DST, Government of India, for providing financial assistance to perform the research work.

References

- Adhikary, K.B., Pang, S., Staiger, M.P., 2008. Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE). *Composites Part B: Engineering* 39 (5), 807–815.
- Ahn, D., Kwon, J.H., Kwon, S., Song, J., Lee, S., 2009. Representation of surface roughness in fused deposition modeling. *Journal of Materials Processing Technology* 209 (15–16), 5593–5600.
- Al-Salem, S.M., Lettieri, P., Baeyens, J., 2010. The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. *Progress in Energy and Combustion Science* 36 (1), 103–129.
- Archard, J.F., 1953. Contact and rubbing of flat surfaces. *Journal of Applied Physics* 24 (8), 981–988.
- Armillotta, A., 2006. Assessment of surface quality on textured FDM prototypes. *Rapid Prototyping Journal* 12 (1), 35–41.
- Bagsik, A., Schöppner, V., 2011. Mechanical properties of fused deposition modeling parts manufactured with Ultem 9085. In: *Proceedings of the 69th Annual Technical Conference of the Society of Plastics Engineers (ANTEC '11)*, Boston, Mass, USA, pp. 1294–1298.
- Bortoloto, E.M., Rovani, A.C., Seriacopi, V., *et al.*, 2013. Experimental and numerical analysis of dry contact in the pin on disc test. *Wear* 301 (1–2), 19–26.
- Boparai, K.S., Singh, R., Singh, H., 2016. Wear behaviour of FDM parts fabricated by composite material feed stock filament. *Rapid Prototyping Journal* 22 (2), 350–357.
- Campbell, G., Spalding, M., 2013. Single-screw extrusion: Introduction and troubleshooting. *Analysing and Troubleshooting Single Screw Extrusion*. 1–22.
- Campbell, G.A., Wang, C., Cheng, H., Bullwinkel, M., te-Riele, M.A., 2001. Investigation of flow rate and viscous dissipation in a single screw pump-extruder. *International Polymer Processing* 16 (4), 323–333.
- Chua, C.K., Leong, K.F., Lim, C.S., 2003. *Rapid Prototyping: Principles and Applications*. Singapore: World Scientific.
- Covas, J.A., Gaspar-Cunha, A., 2001. A computational investigation on the effect of polymer rheology on the performance of a single screw extruder. *Erheopt* 1 (1), 41–62.
- Cunico, M.W.M., 2013. Study and optimisation of FDM process parameters for support-material-free deposition of filaments and increased layer adherence. *Virtual and Physical Prototyping* 8, 127–134.
- Espalin, D., Alberto Ramirez, J., Medina, F., *et al.*, 2014. A review of melt extrusion additive manufacturing processes: I. Process design and modeling. *Rapid Prototyping Journal* 20 (3), 192–204.
- Garg, H.K., Singh, R., 2015. Development of new composite materials for rapid tooling using fused deposition modelling. *Advancement in Manufacturing Process (Special Topic Volume)*, Materials Science Forum 808, 103–108.
- Gebhardt, A., Gibson, I., 2003/2006. *Rapid prototyping: From product development to medicine and beyond*. In: *Virtual and Physical Prototyping*, 1. Munich: Hanser, pp. 31–42.
- Gibson, I., Rosen, D.W., Stucker, B., 2010. *Additive Manufacturing Technologies: Rapid Prototyping to Direct Digital Manufacturing*. New York, NY: Springer.
- Herrera-Franco, P., Valadez-Gonzalez, A., Cervantes-Uc, M., 1997. Development and characterization of a HDPE–sand–natural fiber composite. *Composites Part B: Engineering* 28 (3), 331–343.
- Jen, Y.-M., Huang, C.-Y., 2014. Effect of temperature on fatigue strength of carbon nanotube/epoxy composites. *Journal of Composite Materials* 48 (28), 3469–3483.
- Kennedy, F.E., Lu, Y., Baker, I., 2015. Contact temperatures and their influence on wear during pin-on-disk tribotesting. *Tribology International*, Part B 82, 534–542.
- Lisowski, Z., Stolarski, T.A., 1981. A modified theory of adhesive wear in lubricated contacts. *Wear* 68, 333–345.
- Lu, N., Oza, S., 2013. A comparative study of the mechanical properties of hemp fiber with virgin and recycled high density polyethylene matrix. *Composites Part B: Engineering* 45 (1), 1651–1656.
- Mikulionok, I.O., Radchenko, L.B., 2012. Screw extrusion of thermoplastics: I. General model of the screw extrusion. *Russian Journal of Applied Chemistry* 85 (3), 489–504.
- Nagaraju, B., Ramji, K., Prashad, V.S.R.K., 2011. Studies on tribology properties of ZnO filled polymer nanocomposites. *ARPN Journal of Engineering and Applied Science* 6, 75–82.
- Novak, R., Polcar, T., 2014. Tribological analysis of thin films by pin-on-disc: Evaluation of friction and wear measurement uncertainty. *Tribology International* 74, 154–163.
- Oliveux, G., Dandy, L.O., Leeke, G.A., 2015. Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties. *Progress in Materials Science* 72, 61–99.
- Panda, S.K., 2009. Optimization of fused deposition modelling (FDM) process parameters using bacterial foraging technique. *Intelligent Information Management* 1 (2), 89–97.
- Pham, D.T., Gault, R.S., 1998. A comparison of rapid prototyping technologies. *International Journal of Machine Tools and Manufacturing* 38 (10/11), 1257–1287.
- Rosato, D.V., Knovel (Firm), 1998. *Extruding Plastics: A Practical Processing Handbook*, first ed London: Chapman & Hall.
- Singh, N., 2015. Experimental investigations for mechanical properties of Nylon-6-SiC–Al₂O₃ based feed stock filament for FDM. MTech Thesis, Production Engineering, P.T.U.
- Singh, S., Singh, R., 2016. Effect of process parameters on micro hardness of Al–Al₂O₃ composite prepared using an alternative reinforced pattern in fused deposition modelling assisted investment casting. *Robotics and Computer-Integrated Manufacturing* 37, 162–169.
- Venuvinod, P.K., Ma, W., 2004. *Rapid Prototyping: Lased Based and Other Technologies*. Dordrecht, The Netherlands: Kluwer Academic Publishers.
- Volpato, N. (Ed.), 2007. *Prototipagem rápida: Tecnologias e aplicações (Rapid prototyping Technologies and Applications)*. São Paulo, Brazil: Edgard Blucher.
- Wang, Y., Yu, K.M., Wang, C.C.L., Zhang, Y., 2011. Automatic design of conformal cooling circuits for rapid tooling. *CAD Computer Aided Design* 43 (8), 1001–1010.
- Wohlers, T.T., 2007. *Wohlers Report 2007: Executive Summary, Annual Worldwide Progress Report*. Fort Collins, CO: Wohlers Associates Inc.
- Yildirim, E., Miskolciz, N., Onwudilia, J.A., *et al.*, 2015. Evaluating the mechanical properties of reinforced LDPE composites made with carbon fibres recovered via solvothermal processing. *Composites Part B: Engineering* 78, 393–400.
- Zein, I., Hutmacher, D.W., Tan, K.C., Teoh, S.H., 2002. Fused deposition modeling of novel scaffold architectures for tissue engineering applications. *Biomaterials* 23 (4), 1169–1185.
- Zhong, W., Li, F., Zhang, Z., Song, L., Li, Z., 2001. Short fiber reinforced composites for fused deposition modeling. *Materials Science and Engineering A* 301 (2), 125–130.

Further Reading

- Bedi, P., 2015. Effect of single particle size, double particle size and triple particle size Al_2O_3 in Nylon-6 matrix on mechanical properties of feed stock filament for FDM. Mtech Thesis, Production Engineering, P.T.U.
- Ettles, C.M.M., Shen, J.H., 1988. The influence of frictional heating on the sliding friction of elastomers and polymers. *Rubber Chemistry and Technology* 61, 119–136.
- Singh, S., Singh, R., 2015. Wear modelling of Al- Al_2O_3 functionally graded material prepared by FDM assisted investment castings using dimensionless analysis. *Journal of Manufacturing Processes* 20, 507–514.
- Stephens, B., Azimi, P., Orch, Z.E., Ramos, T., 2013. Ultrafine particle emissions from desktop 3D printers. *Atmospheric Environment* 79, 334–339.

Polymer Twin Screw Extrusion With Filler Powder Reinforcement

Rupinder Singh and Sunpreet Singh, Guru Nanak Dev Engineering College, Ludhiana, India
Mohammed SJ Hashmi, Dublin City University, Dublin, Ireland

© 2017 Elsevier Inc. All rights reserved.

This is a reproduction of Rupinder Singh, Sunpreet Singh, Mohammed S.J. Hashmi, Polymer Twin Screw Extrusion With Filler Powder Reinforcement, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2017, doi:10.1016/B978-0-12-803581-8.04162-X.

Introduction and Literature Review

Single and twin screw extruders (TSEs) have been used by the food industry to produce a variety of products, such as: snack foods, confectioneries, bread, pasta products, pet foods, and breakfast cereals. TSEs are more complex and costly than single screw extruders, but they possess many advantages (Akdogan, 1996). Apart from the food sector, various other industries including pharmaceutical, bioprocessing and technology, and most importantly plastic technology are incomplete when imagined without a TSE. TSEs play a major role in blending, compounding, devolatilization, reactive extrusion, and profile extrusion for various categories of materials. As a matter of fact extruders were first introduced in the plastics and food industries, in the early 20th century (Mollan, 2003), for the production of pipes and pasta products respectively. Gamlen and Eardley (1986) were one of the first to use the TSE in the pharmaceutical field. Nowadays, TSEs are applied in the pharmaceutical field for the manufacture of a variety of dosage forms and formulations such as granules, pellets, tablets, suppositories, implants, stents, transdermal systems, and ophthalmic inserts (Breitenbach, 2002). In the category of TSE, there exist two configurations of screws, corotating and counterrotating, depending upon their relative motions as shown in Fig. 1 (Martin, 2013). However, corotating TSEs were mostly used for research applications (Meijer and Elemans, 1988; Gogoi and Yam, 1994). Screw configuration is realized by a combination of screw elements; for example, feeding, conveying, mixing, or retaining functions are possible.

Due to the inherent characteristics of TSE design, variations made in barrel segments, screw elements and dosing points can be varied to adapt TSE for manufacturing of a large variety of compounds. Typical adaptations are the use of modified screw profiles tailoring the amount of mechanical mixing, residence time and pressure levels, within limits, to specific needs of the material system. Classical conveying or forwarding elements are always inserted at cylinder openings, for example, at barrel holes to convey material away from the feed opening or to discharge processed material at the end of the extruder. Kneading elements or kneading blocks, the second classical element type, are usually used when material has to be sheared and dispersively mixed. Whereas, combing mixer elements meet the challenge of conveying and mixing simultaneously. Basically they are conveying elements with longitudinal slots, without or having almost no loss in forwarding properties (Thiele, 2003). A typical sectional configuration of TSE is shown in Fig. 2.

One of the key factors to achieve desirable properties of the polymer blend is the control of morphology (Bourry and Favis, 1998). Favis and Therrien (1991) studied the morphology of polypropylene (PP) and polycarbonate modified in corotating TSE. It was found that die wall proximity, high composition, and high viscosity/elasticity ratios resulted in the preferential fiber formation in the dispersed phase. Viscosity ratio effect on phase size between TSE and an internal mixing chamber indicated a significantly coarser dispersed phase in the latter case at high viscosity ratio. However, at a lower viscosity ratio the phase size and size distribution were identical in the two processing environments. Machado *et al.* (1999) monitored the chemical conversion and morphological evolution of PA-6/EPM/EPM-g-MA blends along a TSE by quickly collecting small samples from the melt at specific barrel locations. The results show that the MA content of all blends decreases drastically in the first zone of the extruder. The extruder was found to produce insignificant changes in morphology. Sui *et al.* (2009) prepared a novel plant fiber reinforced PP composite by using a corotating TSE. It was found that there existed no filler's agglomerations, which indicated that blending by means of the TSE was an effective means for dispersing the plant fibers in the polymer matrix. In another work, Ohtsubo *et al.* (2005) developed a novel foodstuff from pregerminated brown rice through a TSE. The rice samples were subjected to extrusion cooking, immediately after the germination and adjustment of the moisture contents. Lertwimolnun and Vergnes (2006) used corotating TSE for the preparation of PP/organoclay nanocomposites with maleic-anhydride as compatibilizer. They investigated the effects of processing conditions as well as screw profile of TSE in response of forming PP nanocomposites. It has been found that the proportion of exfoliation was dependent on screw speed and feed rate. Peltola *et al.* (2006) also studied the effect of screw speed on morphology, rheological, and mechanical properties of nano-clay reinforced PP nanocomposites with aid of transmission electron microscopy, thermogravimetric analysis, rheometry, and mechanical test. The results of the study highlighted that nanocomposites showed both intercalated and exfoliated structures depending on the screw speeds of the extruder. Hsieh *et al.* (1989) also considered screw speed as one of the input parameters for processing of corn meal. Jesus *et al.* (2016) blended poly (L-lactic acid) (PLA) and silver (Ag) particles through melt processing by using a TSE. The concentration of silver particles in nanocomposites were kept at 0.1, 0.2, and 0.3 wt%, which resulted in enhancement of thermal and mechanical properties of poly (L-lactic acid). Fig. 3 shows the results of thermal and mechanical properties of the TSE processed nanocomposites.

It has been found that with an increase in the wt% of Ag nanoparticles in PLA the resulting heat capacity of the nanocomposite wires was increased, while on the other side their tensile strength was decreased. Further, it is highlighted here that the TSE processed PLA attained more heat capacity compared to unprocessed PLA while maintaining its tensile strength. Lee and Han (2000) conducted

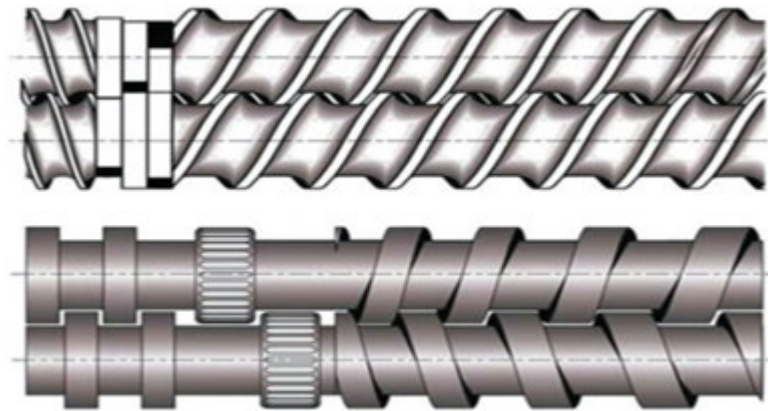


Fig. 1 Corotating and counterrotating intermeshing twin screw extruder (TSE) geometries (Martin, 2013).

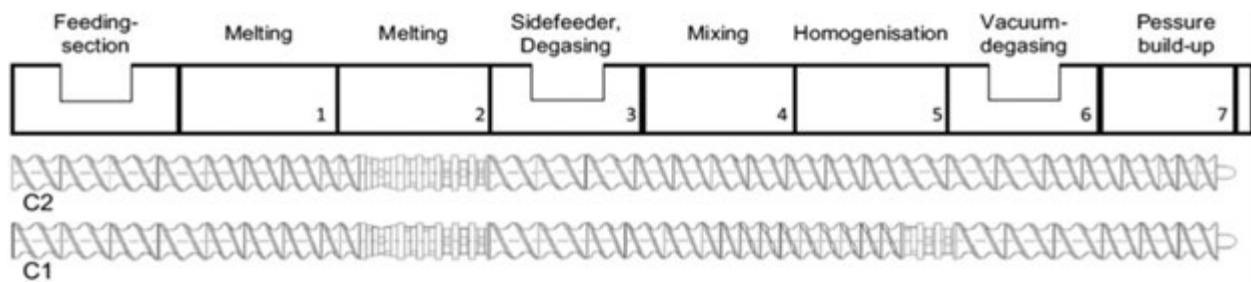


Fig. 2 Section configuration of twin screw extruder (TSE). Reproduced from Feldmann, M., Heim, H.P., Zarges, J.C., 2016. Influence of the process parameters on the mechanical properties of engineering biocomposites using a twin-screw extruder. *Composites: Part A* 83, 113–119.

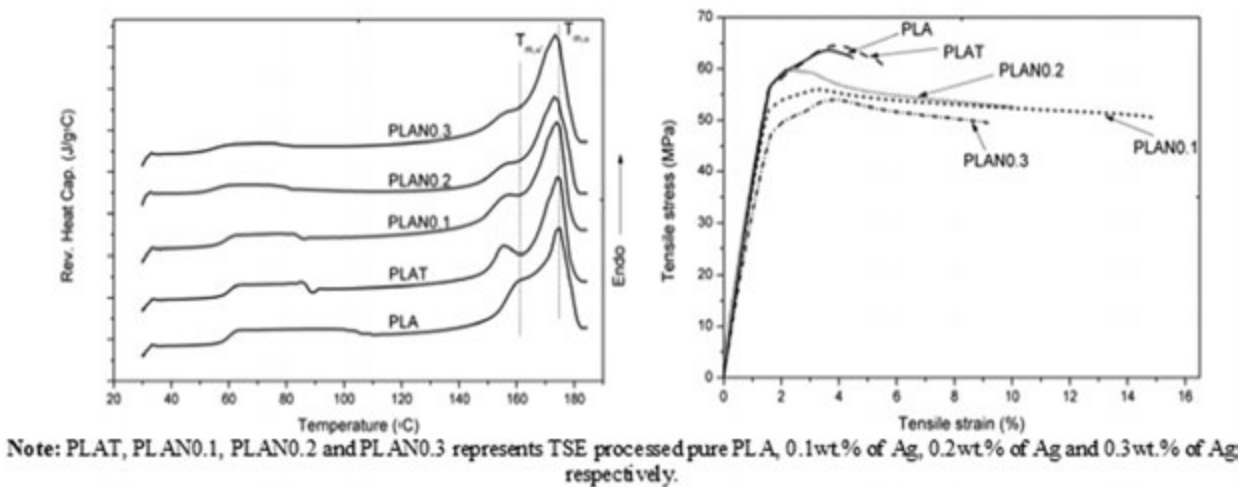


Fig. 3 Thermal and mechanical properties of twin screw extruder (TSE) processed nanocomposites. Reproduced from Jesus, E., Bautista-Del, A., Ana, B., *et al.*, 2016. Enhancement of crystallinity and toughness of poly (L-lactic acid) influenced by Ag nanoparticles processed by twin screw extruder. *Polymer Composites*. doi:10.1002/pc.24217.

a “screw pullout” experiment and investigated the evolution of blend morphology, determined by scanning electron microscopy, along the TSE axis by putting emphasis on the effects of viscosity ratio, blend composition, and processing variables (barrel temperature profile and screw speed). Four blend systems based on the difference in the melting temperature, namely, polystyrene (PS)/poly(methyl-methacrylate), PS/polycarbonate, PS/high-density polyethylene, and PS/PP, were selected. The results of their study outlined the capability of TSE for uniform blending. Biobased polyamide was reinforced with 20 and 30% chopped cellulosic fiber (by wt%), with corotating TSE, for addressing important applications of material science and meeting the rising demand for

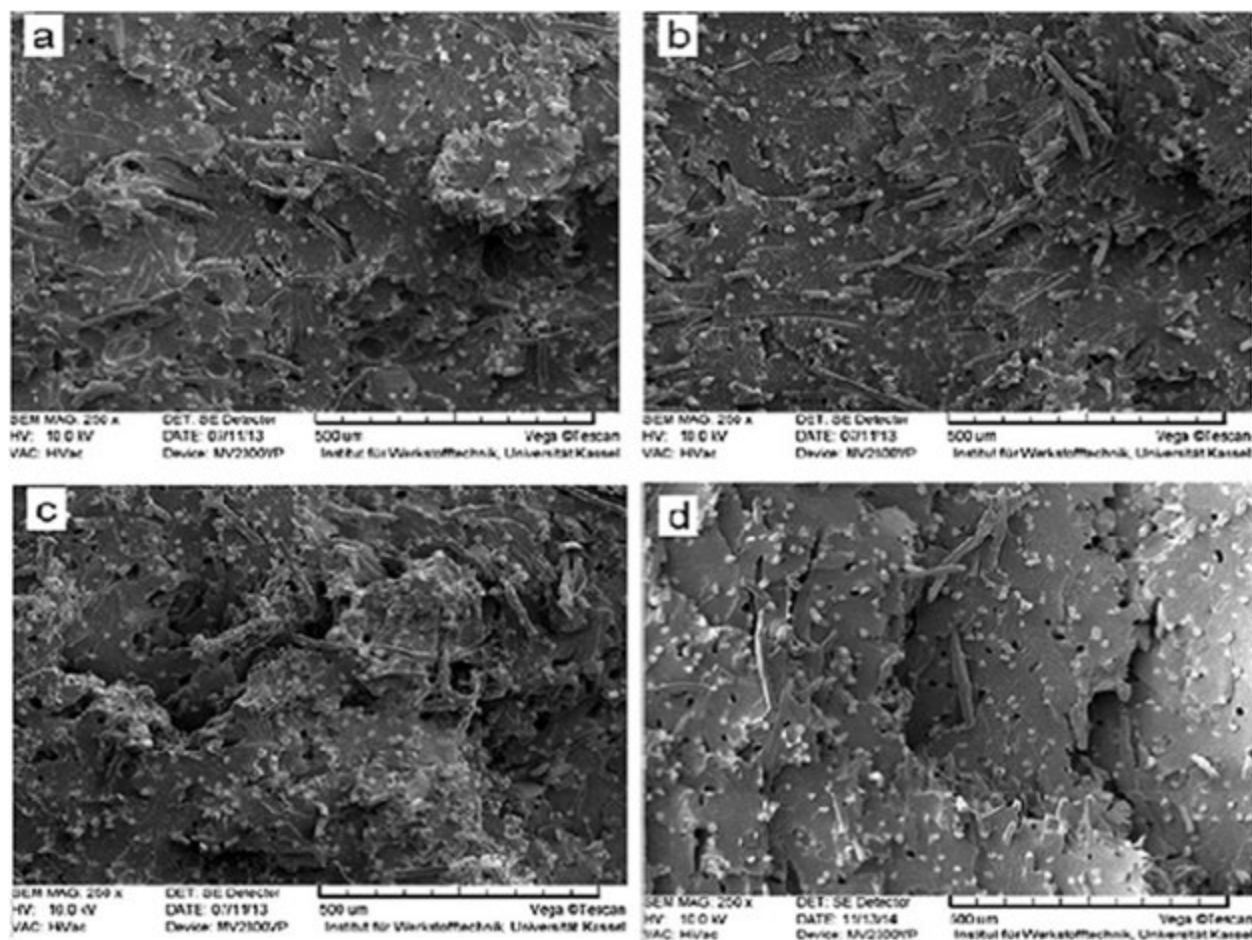


Fig. 4 Fiber distribution and fiber pullout in compounds with 20 wt% fiber content processed using different screw configurations. Twin screw extruder (TSE) configuration C1 (a), configuration C2 (b), single-screw extruder at T1 temperature profile (c), and configuration C2 at T2 temperature profile (d) (Reproduced from Feldmann, M., Heim, H.P., Zarges, J.C., 2016. Influence of the process parameters on the mechanical properties of engineering biocomposites using a twin-screw extruder. Composites: Part A 83, 113–119.) (Note: T1 and T2 are the temperature profiles of screw as given in Feldmann *et al.* (2016)).

sustainable materials (Feldmann *et al.*, 2016). The micrographical analysis shows the effect of screw configuration on the distribution of the cellulose fibers in the matrix material. Compounds prepared with TSE (refer to Fig. 4(a), (b), and (d)) and single screw extruder (refer to Fig. 4(c)) were compared.

It has been found that there was no significant difference in the fiber distribution, which indicated some agglomerates due to the lack of mixing elements and kneading disks in screw configurations C1 and C2 as shown in Fig. 2. Villmow *et al.* (2008) used corotating TSE for dispersion of multiwalled carbon nanotubes in PLA. The composites were prepared with four different proportions of carbon nanotubes, screw profile, temperature profile, and rotation speed under different processing conditions. Transmission electron microscopy was performed to observe the dispersion and network formation in the submicron scale. High rotation speed that ensured a certain residence time of the melt combined with a screw profile containing mainly mixing elements were found to be highly convenient to disperse and distribute the nanotubes in PLA. Similarly Jonooobi *et al.* (2010) developed cellulose nanofiber (1, 3, and 5% by wt.%) reinforced PLA by TSE. Morphology, mechanical, and dynamic mechanical properties were studied theoretically and experimentally to see how different cellulose nanofiber concentrations affected the properties. It has been found that the tensile modulus and strength increased from 2.9 to 3.6 GPa and from 58 to 71 MPa, respectively (for 5 wt%). Further dynamic mechanical test showed that the storage modulus increased for all nanocomposites as compared to PLA. Verma (2016) discussed about the nanoclay reinforcement in a polymer matrix and its effect on various mechanical properties such as tensile strength, tensile modulus, flexural strength, flexural modulus, impact strength, etc. Recently, Upasani *et al.* (2016) used TSE for the preparation of ZnO/MWCNT/PP composite films, which were characterized by differential scanning calorimetry (DSC), thermal gravimeter, reflectance, X-ray diffraction analysis, and scanning electron microscopy. The composite films showed antibacterial and antifungal properties, improved fire resistance, and lower combustion toxicity compared to neat PP film. Along with this, camouflage applications and very good antistatic properties made these films suitable for multiple hazard protections. From the literature review, it has been found that there exist many processing variables on which the quality characteristics of the

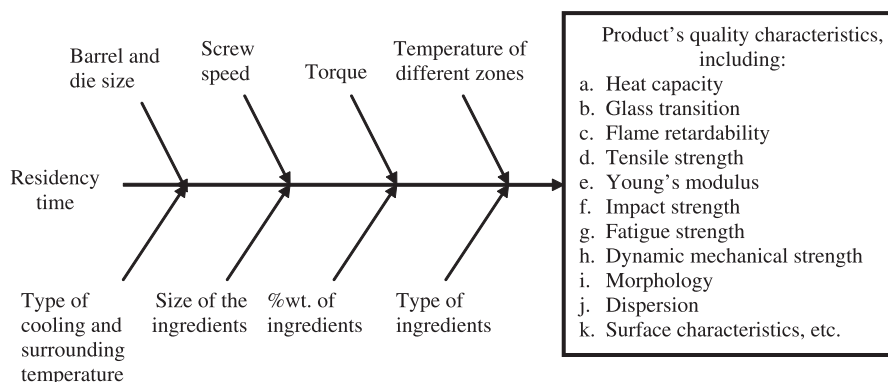


Fig. 5 Fish bone diagram relation between twin screw extruder (TSE) parameters and product's quality characteristics.

resulting blend/composite/film depend. **Fig. 5** shows the fishbone diagram highlighting the important input variables for product quality.

Extrusion of Polymeric Composite Feedstock

Polymer nanocomposites are an emerging class of materials that have properties that are often superior to conventional composites and may be synthesized using surprisingly simple and inexpensive techniques. For about a half century, an extensive research effort has been witnessed in the incorporation of metal nanoparticles into a polymer matrix. This interest arises in polymer composites since they can preserve the mechanical properties of the polymer matrix but can benefit in heat conduction properties due to the inclusion of metal fillers (Gul and Shenfill, 1984). Among the various nanosized metal particles, gold and silver were frequently used as nanofillers for polymer matrices due to their good conductivity and chemical stability (Zhu *et al.*, 2016). Nanoparticle composites contributed to the development of future data storage, optical and electrorheological materials or display devices (Schmidt and Malwitz, 2003). Since the documented discovery of carbon nanotubes (CNTs) in 1991 by Iijima (1999) and the realization of their unique physical properties, including mechanical, thermal, and electrical, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of these properties (Biercuk *et al.*, 2002; Ounaies *et al.*, 2003; Weisenberger *et al.*, 2003). CNTs are quite effective compared to traditional carbon black microparticles, primarily due to their large aspect ratios (Colbert, 2003). The properties and applications of CNTs and related materials have been very active research fields over the last decade (Guldi *et al.*, 2005). CNTs possess high flexibility, low mass density, and large aspect ratio (typically >1000), whereas predicted and some experimental data indicate extremely high tensile moduli and strengths for these materials. Individual single-walled carbon nanotubes (SWCNTs) can be metallic or semiconducting. The latter can transport electrons over long lengths without significant interruption, which makes them more conductive than copper (Durkop *et al.*, 2004). The effect of CNT alignment on percolation conductivity in SWCNT/PMMA composites has been investigated by Du *et al.* (2003). The SWCNTs were aligned by melt fiber spinning, and various levels of alignment could be obtained by controlling the extensional flow in the spinning process. SWCNTs consisted of a single graphite sheet seamlessly wrapped into a cylindrical tube whereas multiwalled carbon nanotubes (MWCNTs) comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk (Baughman *et al.*, 2002). Similarly, copper (Cu) nanopowder (CNP) also has a very rich contribution to the development of conductive polymeric composites. Conductive polymer composites have been intensively studied due to their many advantages, including good processability, corrosion resistance, comparatively low weight, and low cost (Li and Sundararaj, 2015). Compared with nanoparticles, nanowires (NWs) have smaller dimension structure and high aspect ratio, which could efficiently transport electrical and thermal carriers along one controllable direction (Hu *et al.*, 1999). Cu in nanorange has recently garnered increasing attention as an excellent candidate for transparent conducting films (Nam and Lee, 2016). Cu has high intrinsic conductivity, and is a potential alternative to indium tin oxide and silver NWs. Cu is only 6% less conductive than silver, and is very abundant and 100 times less expensive than indium tin oxide and silver (Jewell and Kimball, 2014).

The feed stock filament can be produced with two techniques: capillary or piston extrusion and screw extrusion (Seyi *et al.*, 2001). Piston extrusion is used for fabricating filaments in small quantities that are used for trial runs only. Screw extrusion is used for continuous production of filaments. Size of a single screw extruder is specified with screw diameter and L/D ratio. Single screw extrusion is the most cost-effective and effective way to melt and pump a polymer (Pan *et al.*, 2012). The various process variables of the screw extrusion process are screw speed, barrel temperature, die temperature, water tank temperature, and take-up unit speed. The optimum value of all these parameters should be required for the fabrication of a continuous, homogenous, flexible filament with consistent diameter or varying within the limits. Thermocouples are attached at various sections of the screw extruder, to monitor temperature changes during the processing of material. Chamil *et al.* (2011) generated a nonlinear model of die melt temperature profile in order to predict the die temperature with the help of thermocouple mesh and used it for selecting the optimum process setting for improving process homogeneity. For fused deposition modeling (FDM) feedstock filament the

desired value of diameter is 1.75 mm. The feedstock filament generally accomplishes two functions: one is to feed material and second is to act as a piston to force material through a capillary tube. If the filament diameter is less than the desired value, the flow rate of material through the liquefier head becomes low and creates roads with smaller width and thickness. This results in poor bonding between adjacent roads and layers and creates voids and air gaps, which decreases mechanical strength and surface finish of parts. If the diameter is more than the desired value, then either the filament is not fed properly into the liquefier head through the capillary tube or it increases the flow rate of material and decreases dimensional accuracy and surface finish. The overflow of material from the capillary tube may damage the internal circuits of the liquefier head. The circularity or ovality of the diameter should be within limits for continuous feeding and proper gripping of filaments between the rollers. The single screw extrusion process consists of four units: PLC unit, screw extruder, water tank, and take-up unit. The PLC unit contains various electrical circuits and servo drives for the proper coordination and smooth functioning of the extruder. The most important part of the screw extruder is the screw. The conventional single screw extruder, also called a plasticating extruder, is composed of three sections: the feeding section, compression section, and metering section. The material enters inside the barrel through a hopper. The feeding is either by gravity or by screw. In the feed section the material is moved from the hopper and preheated. The heated material is compressed in the compression section and pressure starts building inside the screw barrel. The material is transformed into fluid; air mixed with pellets is extracted from the melt. In all screws at least the first 70% or so of melting is due to the shear stress in the melt film between the barrel and the solid bed surface. In the metering section, the various ingredients of melt are homogeneously mixed and sufficient pressure is developed to pump it through the die opening. Due to high pressure developed inside the barrel, the melt is forced to the die zone. Before reaching the die, the melt passes through a screen pack, a series of wire meshes supported by a stiff plate containing small axial holes. The screen pack performs two functions. The first is to filter out contaminants and hard lumps and the second is to build sufficient pressure in the metering section required for the extrusion process. The pressure is developed during the extrusion process in various sections. Screw design is selected according to the type of material to be processed. The melt pressure developed inside the screw not only depends upon optimum parameters but also on material properties and machine geometry (screw channel depth, barrel diameter, surface conditions of the barrel and screw, barrel thickness). Singh and Singh (2014) developed a cost-effective nylon-based feedstock wire FDM machine. They have intended to replace commercially available ABS with Al_2O_3 reinforced nylon wire without changing any hardware or software in the machine. A single screw extruder was used for wire preparation and wire thus produced was tested on FDM for its mechanical properties, such as tensile strength and percentage elongation. Šafka *et al.* (2016) dealt with specific polymer composites that were modified for FDM. These two phase systems involved thermoplastic matrix filled with natural fibers to put FDM technology on the accuracy of the semiproduct formed into the filament shape. Individual steps of the polymer composite palletization and the following preprocessing and processing activities were described in their work. Sa'ude *et al.* (2016) developed Cu powder filled polymeric composite filament for FDM applications. The dynamic mechanical testing highlighted that the addition of Cu powder resulted in an increase in the storage modulus, loss modulus (E''), and tan delta of the resulting parts. Recently, the company Graphene 3D Lab has proposed a commercial plastic/graphene composite filament for printing of graphene-enhanced plastic structures using a conventional FDM printer (Kim *et al.*, 2015). Recently, it has been reported that the addition of nanomaterials such as carbon nanotubes, NWs and quantum dots to host matrices like polymers, metals, and ceramics via additive manufacturing/3D printing has the potential to enable greater capabilities in nanocomposite production (Campbell and Ivanova, 2013). This could be achieved by either printing the two ingredients side-by-side (i.e., on the previously described geometrical areas) or by premixing of the nanomaterials into the host matrix and followed by 3D printing of the nanocomposite mixture as a complete part. For the first, one needs to modify the hardware or even redesign the deposition strategy along with adjusting computer insight. However, both of the two are not required for the second option but synthesis of the composite filament, having controlled dimensions, could be tedious. This is for sure that the parts produced via second way will possess better mechanical/electrical/thermal properties as compared to the first one since the geometrical features are easily controllable through computer insights.

In this we have developed a composite feedstock filament consisting of biocompatible poly-vinyl-chloride/polypropylene (PVC/PP) blend in 70/30 wt% ratio. This blend was reinforced with 4 wt% of nano hydroxyapatite (n-HAP) filler and mixed in the form of FDM filament with the help of corotating TSE; HaaKE miniCTW (make: Thermo Fishers) as shown in Fig. 6. The high grade PVC and PP were purchased from (Batra polymers, Ludhiana (India)), having melt flow index (MFI) 35–38 g/10 min and 13–17 g/10 min, respectively, were used to prepare a polymer blend that was further reinforced with n-HAP powder (ranges from 53 to 150 nm) as shown in Fig. 7. The n-HAP powder was supplied by Nanoshel, India.

Composite Filament Extrusion

Several methods can be used to produce a uniform filament; one is continuous extrusion to the filament winder, but the filament stuck together and became very thin. Another is a water-bath to quench the filament and maintain the diameter, but the water-bath did not fit directly next to the extruder and the filament still stretched. In this study, we have selected prepared hybrid feedstock composite filaments with different proportions of filler as shown in Table 1. The extrusion parameters were selected on the basis of thermograph of virgin PVC and PP as shown in Fig. 8(a) and (b), respectively. From this graph it has been found that the glass transition and thermal melting of PVC and PP took place between 159 and 163°C, respectively, hence the extrusion temperature for composite feedstock filaments was selected slightly on the higher side, i.e., 180–200°C, due to presence of fillers. Different levels of extrusion speed were also selected and diameter of the feedstock filament was maintained at 1.75 mm.

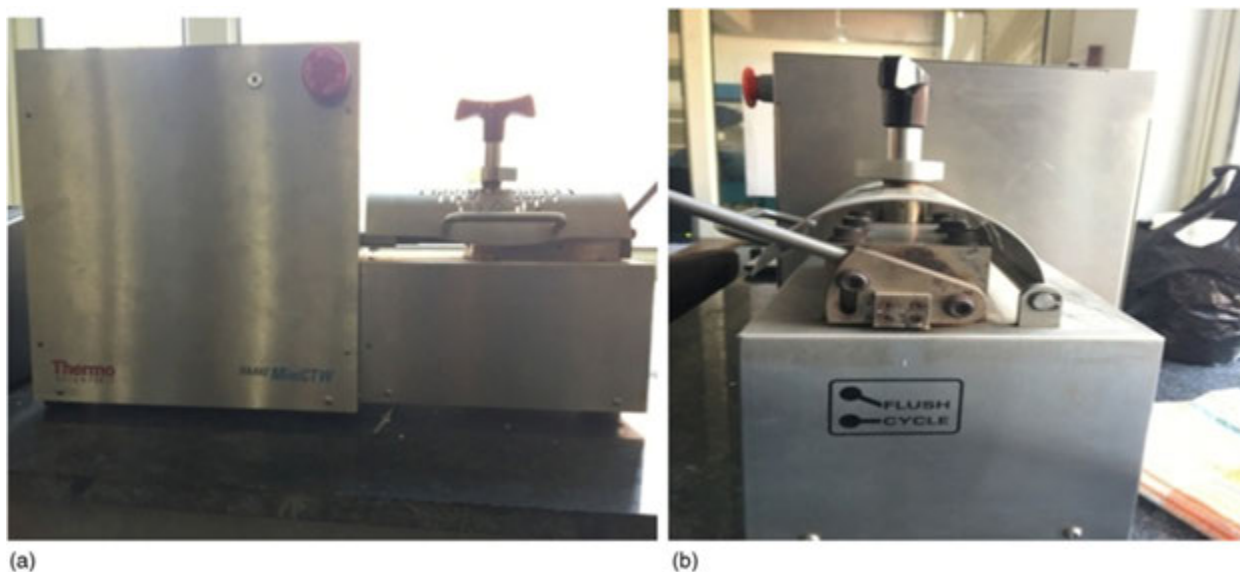


Fig. 6 Side view of twin screw extruder (TSE) (a) and front view of TSE (b). Courtesy: Manufacturing Research Lab, GNDEC, Ludhiana (India).

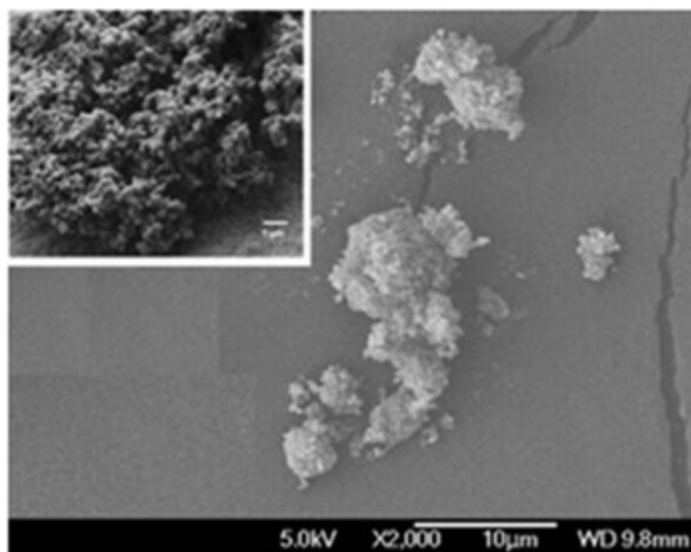


Fig. 7 Micrograph of nano hydroxyapatite (n-HAP).

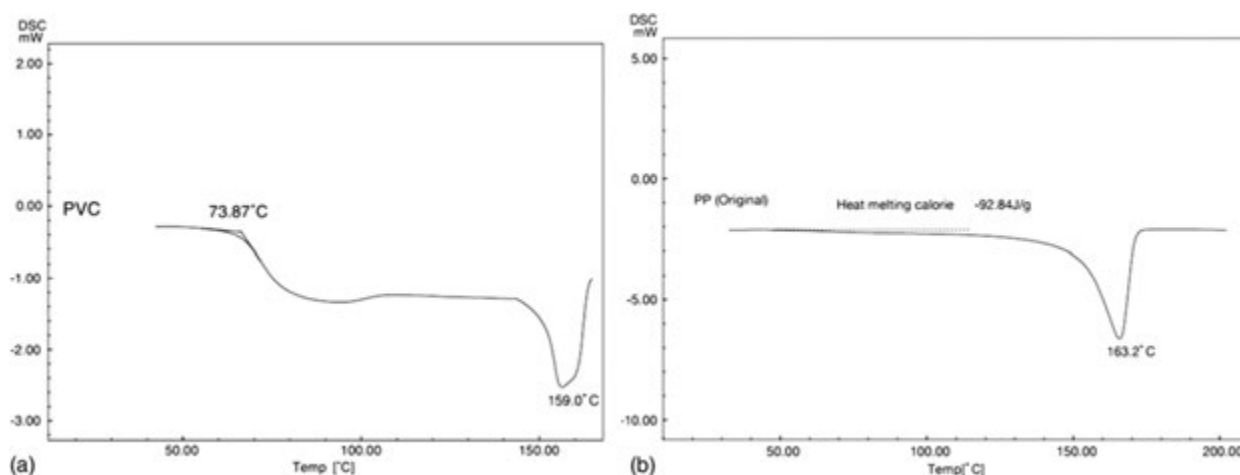
In the present case, a forced convection method was used wherein a fan was cooling the extrudate to fix its dimensions and the windup was carried out manually. Since the mass intake of TSE used in the present study is much less, limited to few grams only, it was not possible to produce a long length of the feedstock filament. However, we were able to develop sufficient lengths of feedstock to fulfill the material consumption by the FDM printer. [Table 1](#) shows the control log of experimentation and [Fig. 9](#) shows the few samples of in-house developed feedstock filament samples.

Rheological Properties of Filament

Rheological properties of the polymeric composites play an important role before allotment of specific application. Oscillatory melt rheology is known to be a very sensitive method to characterize the structure of polymer melts as in literature it described the interconnected structures of anisometric fillers, which led to qualitative changes in the spectra of dynamic moduli and viscosity ([Pötschke et al., 2004](#)). In case of composites with conductive fillers, it has been earlier reported that melt viscosity of the composites was increased whereas variation of processing viscosity was reduced ([Kuan et al., 2005](#)). Recently, the rheological properties of extruded composite filaments were extensively studied with the help of melt flow indexer as per ASTM-D-1238(10)

Table 1 Control log of experimentation (inspired by Taguchi L9 array)

S. No.	Screw speed (rpm)	Extrusion temperature ($^{\circ}\text{C}$)	Extrusion load (kg)
1	30	180	10
2	30	190	15
3	30	200	20
4	40	180	20
5	40	190	10
6	40	200	15
7	50	180	15
8	50	190	20
9	50	200	10

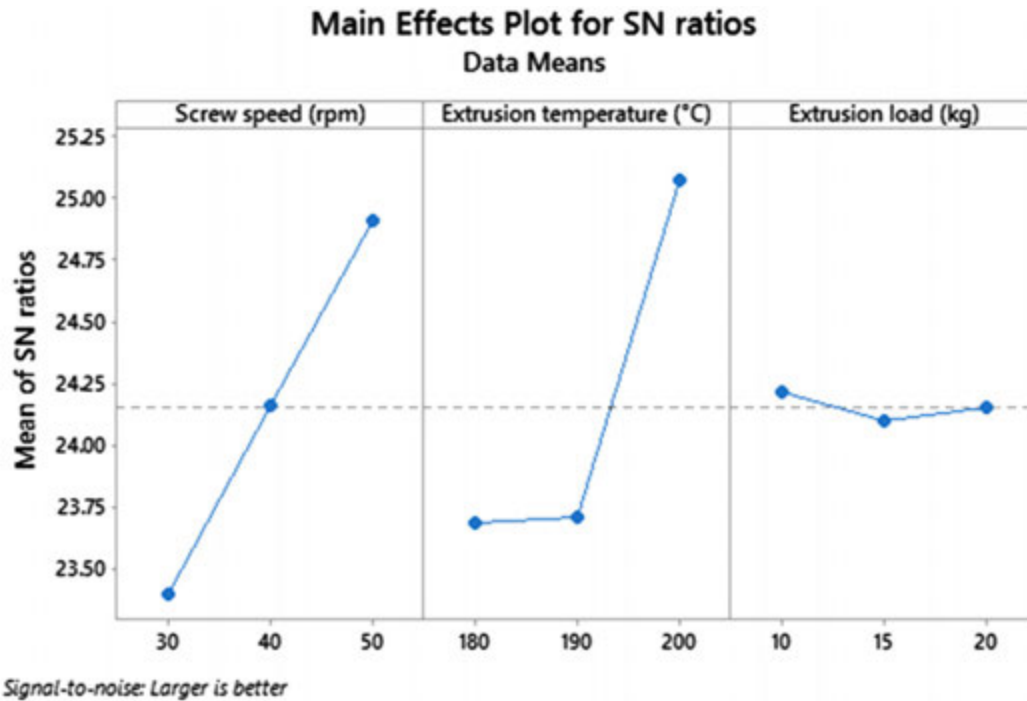
**Fig. 8** Thermograph of poly-vinyl-chloride (PVC) (a) and polypropylene (PP) (b).**Fig. 9** In-house developed feedstock filaments.

standard (Garg and Singh, 2016; Boparai *et al.*, 2016). In the present work, the extruded composite filaments were palletized, manually, and thus used for melt flow analysis. The extrusion weight and temperature were kept constant at 3.8 kg and 220°C respectively. Table 2 shows the output in terms of melt weighed in a 10-min time duration. Fig. 10 shows the S/N response of input process variables on MFI of composite feedstock filament materials.

Fig. 10 outlined that in case of screw speed, with an increase in the speed revolutions the resulting MFI values were increased. This might be due to the fact that during filament preparation with TSE, screw speed enhanced the molecular bonding due to which melting of composite materials in the melt flow indexer took place uniformly. The same trend has been also observed in case of extrusion temperature wherein increase in temperature increased the MFI due to the obvious reasons discussed above. However, extrusion load is found to be unaffected in terms of MFI of the feedstock filaments prepared with TSE. Table 3 shows the

Table 2 Results of melt flow index (MFI)

S. No.	Average MFI (gm/10 min)	S/N ratio (dB)
1	14.35	23.1370
2	13.55	22.6388
3	19.60	24.4022
4	16.34	23.7165
5	15.61	23.8681
6	21.45	24.8905
7	13.19	24.1849
8	12.20	24.6039
9	19.79	25.9289
Overall mean S/N ratio, m		24.15231

**Fig. 10** S/N response of input variables to melt flow index (MFI).

analysis of variance of S/N ratio of input parameters for MFI. From this analysis it has been found that no input parameter has statistical significance for the recorded MFI values at 95% confidence level.

Whereas the percentage contribution of sources; screw speed, extrusion temperature, extrusion load and error is recorded as 45.43, 50.55, 0.26, and 3.75%, respectively. Since the error is less than 5%, it can be outlined that the experimental and measurement errors are within the acceptable range. Further, we have predicted the optimized value of MFI by using the values given in Table 4.

Eq. (1) was used for the prediction of optimized MFI value:

$$\eta_{\text{opt}} = m + (m_{\text{Amax}} - m) + (m_{\text{Bmax}} - m) + (m_{\text{Cmax}} - m) \quad (1)$$

In Eq. (1), “ m ” is overall mean of S/N data (calculated in Table 4); “ m_{Amax} ” is the maximum mean of S/N data for parameter A, i.e., at level 3; “ m_{Bmax} ” is the maximum mean of S/N data for parameter B, i.e., at level 3; and similarly “ m_{Cmax} ” is the maximum mean of S/N data for parameter C, i.e., at level 1. The corresponding optimum MFI value is calculated using Eq. (2):

$$\gamma_{\text{opt}}^2 = 1/10^{-\eta_{\text{opt}}/10} \quad (2)$$

and,

$$\gamma_{\text{opt}} = 19.71 \text{ gm/10 min (predicted value)}$$

For the verification of the calculated value, a confirmatory experiment was performed at the best setting (i.e., A₃B₃C₁) for hardness, which shows 19.79 g/10 min, which is very close to the predicted value.

Table 3 Analysis of variance of S/N ratio for melt flow index (MFI)

Source	Degree of freedom	Sum of square	Variance	Fisher's value	P-value	Contribution (%)
Screw speed (rpm)	2	3.43503	1.71751	12.13	0.076	45.43
Extrusion temperature (°C)	2	3.82251	1.91125	13.49	0.069	50.55
Extrusion load (kg)	2	0.02009	0.01005	0.07	0.934	0.26
Error	2	0.28326	0.14163			3.75
Total	8	7.56089				

Table 4 Response table of S/N ratio for melt flow index (MFI)

Level	Screw speed, A (rpm)	Extrusion temperature, B (°C)	Extrusion load, C (kg)
1	23.68	23.39	24.21
2	23.70	24.16	24.06
3	25.07	24.91	24.15
Delta	1.39	1.51	0.12
Rank	2	1	3

Thermal Analysis of Filament

Mechanical and electrical properties have been extensively studied whereas thermal properties like glass transition temperature, melt enthalpy, degradation at higher temperature, etc., are less investigated. Thermal energy storage in the form of latent heat is one of the most efficient methods for thermal energy storage. Due to high storage density and almost constant temperature during phase transition phase change materials are widely used for storing thermal energy (Dincer and Rosen, 2002; Pielichowska and Pielichowski, 2014). DSC was introduced in the form of commercial instruments during the early 1960s and it has been found to provide a convenient and useful method to measure the glass transition (T_g), enthalpy in melting (ΔH_m) and crystallization temperatures (C_T) of uncured and cured laminates and also the degree of cure of the final product, the heat of reaction during processing. Its main advantages are the modest requirements in terms of sample size (~ 20 mg) and its ability to provide quantitative data on overall reaction kinetics, with relative speed and ease (Barton, 2004). Presently, DSC (make: Mettler Torledo, Switzerland) was used to study the thermal characteristics of resulting composites. Initially thermal test was carried out under dynamic heating as follows: (1) first heating from 30 to 300°C @ 10K/min incremental rate under dry N₂ atmosphere (50 mL/min); (2) first uncontrolled cooling from 300 to 30°C under dry N₂ atmosphere; (3) second heating same as (1); and (4) second cooling same as (2). From Fig. 11, it has been found that the decomposition of the composite mixture took place after 220°C thereby further thermal treatment of steps (2), (3), and (4) did not given any valuable information. In the next iteration, we have modified the thermal treatment of dynamic heating accordingly. So, the rest of the tests were performed as follows: (1) first heating from 30 to 220°C @ 10K/min incremental rate under dry N₂ atmosphere (50 mL/min); (2) first uncontrolled cooling from 220 to 30°C under dry N₂ atmosphere; (3) second heating same as (1); and (4) second cooling same as (2). The respective thermographs are given in appendix A. Here, we have considered the difference of enthalpies of melting during first and second heating as output response. Since it is general fact that some of the polymeric materials started to lose their thermal properties after periodic thermal treatments, in the present case it will be very interesting to understand the effect of TSE parameters on succeeding thermal characteristics of the resulting filament materials. Each time we have recorded some degradation of the polymer composites due to which these materials have taken lesser enthalpy during second heating. Along with this we have also calculated the glass transition temperatures and enthalpy of condensation as given in appendix A. However, melting enthalpy has been only taken into consideration and is studied with response of TSE parameters. The resulting numerical values of ΔH_m ($\Delta H_1 - \Delta H_2$) as given in Table 5 were optimized. From Fig. 12, it has been found that with an increase in the screw speed the ΔH_m value was reduced, which means the resulting composite filament possessed better thermal properties in succeeding heat treatment cycles. This is mainly due to the fact at higher speed the molecular bonding was stronger as compared to lower speed. In this case, extrusion temperature did not play an important role since the slope for this parameter is lying along the mean line. However, in case of extrusion load, it has been found that the ΔH_m values were increased with an increase in the extrusion load. It is difficult to explain the reason behind this trend without performing spectroanalysis, which is part of our upcoming research. From analysis of variance, given in Table 6, it has been found that no input parameter has statistical significance for the recorded ΔH_m values at 95% confidence level.

For this response parameter, optimized value was also calculated by using the values of Table 7.

Eq. (1) was used for predicting optimized S/N ration of ΔH_m . The corresponding optimum hardness value is calculated using Eq. (3):

$$\gamma_{\text{opt}}^2 = 1/10^{\eta_{\text{opt}}/10} \quad (3)$$

$$\gamma_{\text{opt}} = 0.46 \text{ J/gm (predicted value)}$$



Fig. 11 Thermograph for sample 1 of Table 1. DSC, Differential scanning calorimetry.

Table 5 Results of ΔH_m

S. No.	ΔH_m (J/gm)	S/N ratio (dB)
1	1.43	-3.1067
2	1.81	-5.1536
3	3.23	-10.1841
4	1.8	-5.1055
5	3.39	-10.6040
6	0.7	-3.0980
7	1.05	-0.4238
8	0.55	-5.1927
9	0.98	-0.1755
Overall mean S/N ratio, m		-4.78266

For the verification of the calculated value, a confirmatory experiment was performed at the best setting (i.e., $A_3B_3C_1$) for ΔH_m , which shows 044 J/gm, which is very close to the predicted value.

Peak Strength

The peak strength of the in-house extruded feedstock filaments was tested according to ASTM-D412 standard. Specimen sample for tensile testing is shown in Fig. 13, and was tested on a universal testing machine (make: Shanta Engineering, Pune). The results of the tensile test are summarized in Table 8. Fig. 14 shows the S/N response of input process variables on peak strength of the resulting composite filaments. From Fig. 14, it has been found that variation in parametric levels of screw speed did not have any effect on the output response. However, in case of extrusion temperature it has been found that with an increase in the temperature the peak strength of the extruded filaments was also increased. This can be explained by the fact that at higher temperature the mixing of the n-HAP powder particles in polymeric blend is more uniform as compared to the lower levels of the temperatures. The better mixing or uniform distribution of n-HAP particles resulted in improved mechanical properties under tensile load. Further, in case of extrusion load a minor dip has been observed while increasing the extrusion load from 10 to 15 kg. However, further increase in extrusion load resulted in an increase in the peak strength. Table 7 shows the analysis of variance of S/N ratio for

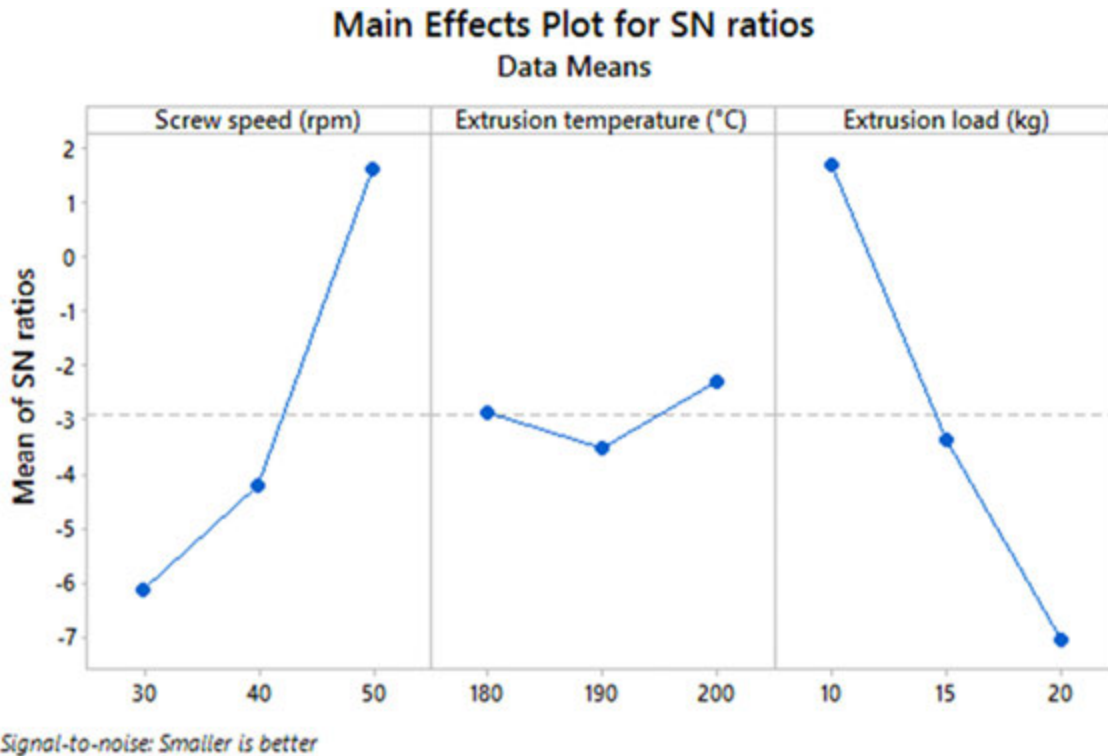


Fig. 12 S/N response of input variables to ΔH_m .

Table 6 Analysis of variance of S/N ratio for ΔH_m

Source	Degree of freedom	Sum of square	Variance	Fisher's value	P-value	Contribution (%)
Screw speed (rpm)	2	98.807	49.404	4.63	0.178	41.23
Extrusion temperature (°C)	2	2.228	1.114	0.10	0.905	0.93
Extrusion load (kg)	2	117.076	58.538	5.49	0.154	48.89
Error	2	21.342	10.671			8.9
Total	8	239.453				

Table 7 Response of S/N ratio for ΔH_m

Level	A (rpm)	B (°C)	C (kg)
1	-6.148	-2.879	-1.728
2	-4.204	-3.522	-3.361
3	-1.648	-2.304	-7.071
Delta	7.796	1.218	8.799
Rank	2	3	1

input variables. From this table, we have found that only extrusion temperature is significantly affecting the peak strength as its p -value is less than 0.05, highlighting its significance at 95% confidence level. Overall from these results, we have come to understand that extrusion speed and extrusion load are not relevant parameters as far as the peak strength of the composite polymer feedstock is concerned.

From Table 9, it has been found that the percentage contribution of screw speed, extrusion temperature, extrusion load and error is 0.09, 77.92, 18.92, and 3.01%, respectively. The contribution of error (less than 5%) here signifies that the experimental errors incurred during part preparation and testing are under control.

Similarly, we have predicted the optimized value of peak strength of composite feedstock filament by using the values given in Table 10, as per Eq. (1).

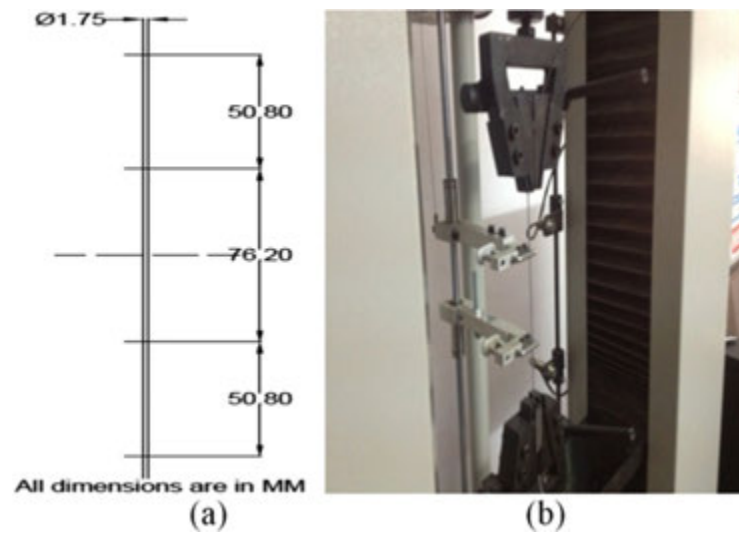


Fig. 13 Universal testing setup; (a) specimen dimension and (b) testing of sample.

Table 8 Results of peak strength

S. No.	Peak strength (MPa)	S/N ratio (dB)
1	16.6	24.4022
2	19.1	25.6207
3	23.0	27.2346
4	16.9	24.5577
5	20.1	26.0639
6	21.1	26.4856
7	18.6	25.3903
8	19.1	25.6207
9	20.1	26.0639
Overall mean S/N ratio, m		25.7155

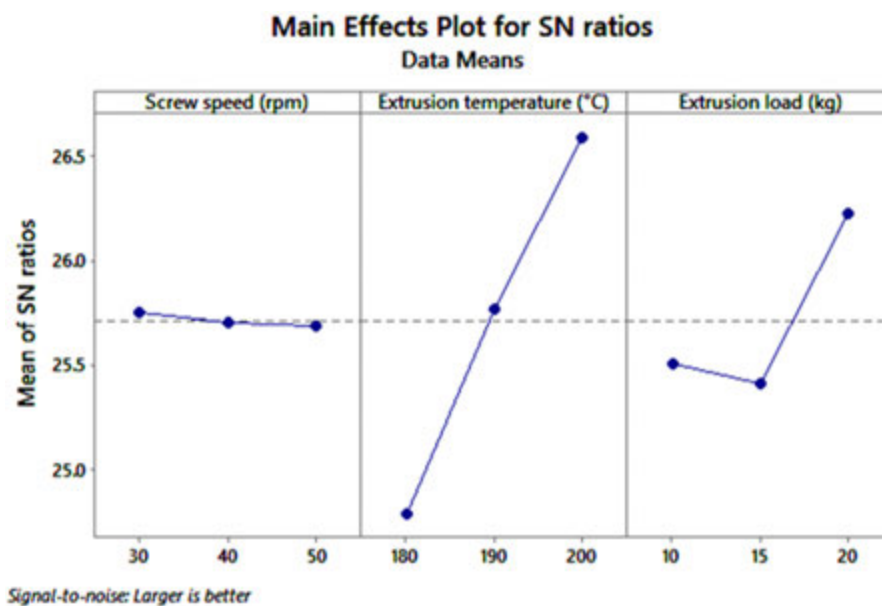


Fig. 14 S/N response of input variables to peak strength.

Table 9 Analysis of variance of S/N ratio for peak strength

Parameters	Degree of freedom	Sum of square	Variance	Fisher's value	P-value	Contribution (%)
Screw speed (rpm)	2	0.00632	0.00316	0.03	0.968	0.09
Extrusion temperature (°C)	2	4.93394	2.46697	25.80	0.037	77.92
Extrusion load (kg)	2	1.20103	0.60052	6.28	0.137	18.92
Error	2	0.19121	0.09560			3.01
Total	8	6.33251				

Table 10 Response table of S/N ratio for peak strength

Level	A (rpm)	B (°C)	C (kg)
1	25.75	24.78	25.50
2	25.70	25.77	25.40
3	25.69	26.59	26.23
Delta	0.06	1.81	0.82
Rank	3	1	2

We got the optimized value of peak strength from Eq. (2):

$$\gamma_{\text{opt}} = 22.73 \text{ MPa (predicted value)}$$

Similarly, the predicted value was verified by performing a confirmatory experiment at optimized settings of input variables, i.e., A₁B₃C₃, which resulted in peak strength of 22.62 MPa, very close to the predicted value.

End Note

TSE has brought a revolution in material extrusion in tasks like compounding/blending of suitable proportions of different ingredients as practiced in the area of pharmaceuticals, polymer technology, food processing, bioprocessing and technology, etc. It has been found that TSE process parameters have a valuable effect on the various mechanical properties (such as tensile strength, tensile modulus, flexural strength, flexural modulus, impact strength, etc.) of reinforced polymer extrudate. In the present article we have developed n-HAP reinforced PVC/PP blended feedstock filaments for FDM applications. A design of experiment was employed to find out the effect of TSE parameters on rheological, mechanical, and thermal properties of extruded filaments. From this article, we have come to know that only extrusion temperature has significantly affected the peak strength of the filament whereas all other output responses were unaffected by input variables of the TSE. The mathematical model developed to predict the optimized values of output responses was thoroughly verified through performing confirmation experiments. Future research efforts are focused on in-depth investigation of the morphology of the produced feedstock filaments.

Acknowledgment

For the present article, the authors are highly grateful to the Science and Engineering Research Board (DST, GoI) for providing us financial support and to our postgraduate students Nishant Ranjan and Ravinder Sharma for their help while doing experimental work.

Appendix A

Differential scanning calorimetry (DSC)-based thermal plots for polymeric composites developed as per Table 1.

References

- Akdogan, H., 1996. Pressure, torque, and energy responses of a twin screw extruder at high moisture contents. *Food Research International* 29, 423–429.
- Barton, J.M., 2004. The application of differential scanning calorimetry (DSC) to the study of epoxy resins curing reactions. *Advanced Topics in Characterization of Composites* 72, 111–154.
- Baughman, R.H., Zakhidov, A.A., de-Heer, W.A., 2002. Carbon nanotubes – The route toward applications. *Science* 297, 787.
- Biercuk, M.J., Llaguno, M.C., Radosavljevic, M., Hyun, J.K., Johnson, A.T., 2002. Carbon nanotube composites for thermal management. *Applied Physics Letters* 80, 15–20.

- Boparai, K.S., Singh, R., Fabbrocino, F., Fraternali, F., 2016. Thermal characterization of recycled polymer for additive manufacturing applications. *Composites Part B: Engineering* 106, 42–47.
- Bourry, D., Favis, B.D., 1998. Morphology development in a polyethylene/polystyrene binary blend during twin-screw extrusion. *Polymer* 39, 1851–1856.
- Breitenbach, J., 2002. Melt extrusion: From process to drug delivery technology. *European Journal of Pharmaceutics and Biopharmaceutics* 54, 107–117.
- Campbell, T.A., Ivanova, O.S., 2013. 3D printing of multifunctional nanocomposites. *Nano Today* 8 (2), 119–120.
- Chamil, A., Kang, L., Marion, M., *et al.*, 2011. A new model based approach for the prediction and optimization of thermal homogeneity in single screw extrusion. *Control Engineering Practice* 19 (8), 862–874.
- Colbert, D.T., 2003. Single-wall nanotubes: A new option for conductive plastics and engineering polymers. *Plastics, Additives and Compounding* 2003, 18–25.
- Dincer, I., Rosen, M.A., 2002. *Thermal Energy Storage: Systems and Applications*. Chichester: Wiley.
- Du, F.M., Fischer, J.E., Winey, K.I., 2003. Coagulation method for preparing single-walled carbon nanotube/poly(methyl methacrylate) composites and their modulus, electrical conductivity, and thermal stability. *Journal of Polymer Science Part B: Polymer Physics* 41 (24), 3333–3338.
- Durkop, T., Kim, B.M., Fuhrer, A.M.S., 2004. Properties and applications of high-mobility semiconducting nanotubes. *Journal of Physics: Condensed Matter* 16, 553–580.
- Favis, B.D., Therrien, D., 1991. Factors influencing structure formation and phase size in an immiscible polymer blend of polycarbonate and polypropylene prepared by twin-screw extrusion. *Polymer* 32, 1474–1481.
- Feldmann, M., Heim, H.P., Zarges, J.C., 2016. Influence of the process parameters on the mechanical properties of engineering biocomposites using a twin-screw extruder. *Composites: Part A* 83, 113–119.
- Gamlen, M.J., Eardley, C., 1986. Continuous extrusion using a Baker Perkins MP50 (multipurpose) extruder. *Drug Development and Industrial Pharmacy* 12, 1701–1713.
- Garg, H., Singh, R., 2016. Investigations for melt flow index of Nylon6-Fe composite based hybrid FDM filament. *Rapid Prototyping Journal* 22 (2), 338–343.
- Gogoi, B.K., Yam, K.L., 1994. Relationships between residency time and process variables in a corotating twin screw extruder. *Journal of Food Engineering* 21, 177–196.
- Gul, V.E., Shenfill, L.Z., 1984. *Conductive Polymer Composites*. Moscow: Khimia.
- Guldi, D.M., Rahman, G.M.A., Zerbetto, F., Prato, M., 2005. Carbon nanotubes in electron donor acceptor nanocomposites. *Accounts of Chemical Research* 38, 871–878.
- Hsieh, F., Mulvaney, S.J., Huff, H.E., Lue, S., Brent Jr., J., 1989. Effect of dietary fiber and screw speed on some extrusion processing and product variables. *Lebensmittel-Wissenschaft & Technologie* 22, 204–207.
- Hu, J., Odom, T.W., Lieber, C.M., 1999. Chemistry and physics in one dimension: Synthesis and properties of nanowires and nanotubes. *Accounts of Chemical Research* 32 (5), 435–445.
- Iijima, S., 1999. Helical microtubules of graphitic carbon. *Nature* 354, 56–58.
- Jesus, E., Bautista-Del, A., Ana, B., *et al.*, 2016. Enhancement of crystallinity and toughness of poly (L-lactic acid) influenced by Ag nanoparticles processed by twin screw extruder. *Polymer Composites*. doi:10.1002/pc.24217.
- Jewell, S., Kimball, S., 2014. *Mineral Commodity Summaries*. Reston, VA: US Geological Survey.
- Jonoobi, M., Harun, J., Mathew, A.P., Oksman, K., 2010. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Composites Science and Technology* 70, 1742–1747.
- Kim, J.H., Chang, W.S., Kim, D., *et al.*, 2015. 3D printing of reduced graphene oxide nanowires. *Advanced Materials* 27 (1), 157–161.
- Kuan, H.C., Ma, C.C.M., Chang, W.P., *et al.*, 2005. Synthesis, thermal, mechanical and rheological properties of multiwall carbon nanotube/waterborne polyurethane nanocomposite. *Composites Science and Technology* 65 (11), 1703–1710.
- Lee, J.K., Han, C.D., 2000. Evolution of polymer blend morphology during compounding in a twin-screw extruder. *Polymer* 41, 1799–1815.
- Lertwimolnun, W., Vergnes, V., 2006. Effect of processing conditions on the formation of polypropylene/organoclay nanocomposites in a twin screw extruder. *Polymer Engineering and Science* 46, 315–323.
- Li, Y., Sundararaj, U., 2015. Comparative study on electrical properties of copper nanowire/polypropylene and carbon nanotube/polypropylene composites. *AIChE Journal* 61 (1), 296–303.
- Machado, V., Covas, J.A., Duin, M.V., 1999. Chemical and morphological evolution of PA-6/Epm/Epm-g-MA Blends in a twin screw extruder. *Journal of Polymer Science: Part A: Polymer Chemistry* 37, 1311–1320.
- Martin, C., 2013. Twin screw extrusion for pharmaceutical processes. In: Repka, M.A., Langley, N., DiNunzio, J. (Eds.), *Melt Extrusion – Materials, Technology and Drug Product Design*. New York, NY: Springer-Verlag, pp. 47–79. (Chapter 2, ISBN 978-1-4614-8431-8).
- Meijer, H.E.H., Elemans, P.H.M., 1988. The modeling of continuous mixers. Part I: The corotating twin-screw extruder. *Polymer Engineering and Science* 28, 275–290.
- Mollan, M., 2003. Historical Overview. In: Ghebre-Sellasie, I., Martin, C. (Eds.), *Pharmaceutical Extrusion Technology*. New York, NY: Marcel Dekker, pp. 1–18.
- Nam, V.B., Lee, D., 2016. Copper nanowires and their applications for flexible, transparent conducting films: A review. *Nanomaterials* 6 (3), 47.
- Ohtsubo, K., Suzuki, K., Yasui, Y., Kasumi, T., 2005. Bio-functional components in the processed pre-germinated brown rice by a twin-screw extruder. *Journal of Food Composition and Analysis* 18, 303–316.
- Ounaies, Z., Park, C., Wise, K.E., Siochi, E.J., Harrison, J.S., 2003. Electrical properties of single wall carbon nanotube reinforced polyimide composites. *Composites Science and Technology* 63, 1637–1646.
- Pan, L., Jia, M.Y., Wang, K.J., Jin, Z.M., 2012. Studies on positive conveying in helically channeled single screw extruders. *Express Polymers Letters* 6 (7), 543–560.
- Peltola, P., Valipakka, E., Vuorinen, J., Syrjala, S., Hanhi, K., 2006. Effect of rotational speed of twin screw extruder on the microstructure and rheological and mechanical properties of nanoclay-reinforced polypropylene nanocomposites. *Polymer Engineering and Science* 46, 995–1000.
- Pielichowska, K., Pielichowski, K., 2014. Phase change materials for thermal energy storage. *Progress in Materials Science* 65, 67–123.
- Pötschke, P., Abdel-Goad, M., Alig, I., Dudkin, S., Lellinger, D., 2004. Rheological and dielectrical characterization of melt mixed polycarbonate-multiwalled carbon nanotube composites. *Polymer* 45 (26), 8863–8870.
- Šafka, J., Ackermann, M., Bobek, J., *et al.*, 2016. Use of composite materials for FDM 3D print technology. *Materials Science Forum* 862, 174–181.
- Sa'ade, N., Ibrahim, M., Ibrahim, M.H.I., 2016. Melt flow rate (MFR) of abs-copper composite filament by fused deposition modeling (FDM). *ARPN Journal of Engineering and Applied Sciences* 11 (10), 6562–6567. ISSN 1819-6608.
- Schmidt, G., Malwitz, M.M., 2003. Properties of polymer-nanoparticle composites. *Current Opinion in Colloid & Interface Science* 8 (1), 103–108.
- Seyi, O., Susmita, B., Amit, B., 2001. Fused deposition of ceramics (FDC) and composites. In: *Proceeding of SFF symposium held in Austin, Texas, August 6–8, 2001*, pp. 224–232.
- Singh, R., Singh, S., 2014. Development of nylon based FDM filament for rapid tooling application. *Journal of the Institution of Engineers (India): Series C* 95, 103–108.
- Sui, G., Fuqua, M.A., Ulven, C.A., Zhong, W.H., 2009. A plant fiber reinforced polymer composite prepared by a twin-screw extruder. *Bioresource Technology* 100, 1246–1251.
- Thiele, W., 2003. Twin-screw extrusion and screw design for pharmaceutical applications. In: Ghebre-Sellasie, I., Martin, C. (Eds.), *Pharmaceutical Extrusion Technology*. New York, NY: Marcel Dekker, pp. 69–99.
- Upasani, P., Sreekumar, T.V., Gaikar, V.G., Jha, J., 2016. Preparation of ZnO/MWCNT/PP composite film and its application as multifunctional protective film. *Polymer Composites*. doi:10.1002/pc.23916.
- Verma, D., 2016. Processing techniques of nanoclay based natural fibre reinforced polymer composites. In: Jawaid, M., *et al.* (Eds.), *Nanoclay Reinforced Polymer Composites, Engineering Materials*. Singapore: Springer Science + Business Media, pp. 209–237.
- Villmow, T., Pötschke, P., Pegel, S., Haussler, I., Kretzschmar, B., 2008. Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix. *Polymer* 49, 3500–3509.

- Weisenberger, M.C., Grulke, E.A., Jacques, D., Rantell, T., Andrews, R., 2003. Enhanced mechanical properties of polyacrylonitrile/multiwall carbon nanotube composite fibers. *Journal of Nanoscience and Nanotechnology* 3 (6), 535–539.
- Zhu, D., Yu, W., Du, H., *et al.*, 2016. Thermal conductivity of composite materials containing copper nanowires. *Journal of Nanomaterials*. doi:10.1155/2016/3089716.

Further Reading

- Bauhofer, W., Kovacs, J.Z., 2008. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology*. doi:10.1016/j.compscitech.2008.06.018.
- Charlie, M., Twin screw extrusion for pharmaceutical processes, Chapter 2 of melt extrusion. In: Repka, M.A. *et al.* (Eds.), *AAPS Advances in the Pharmaceutical Sciences Series 9*. doi: 10.1007/978-1-4614-8432-5_2.
- Hsieh, F., Peng, I.C., Huff, H.E., 1990. Effects of salt, sugar and screw speed on processing and product variables of corn meal extruded with a twin-screw extruder. *Journal of Food Science* 55, 224–227.
- Sa'ude, N., Masood, S.H., Nikzad, M., Ibrahim, M., Ibrahim, M.H.I., 2013. Dynamic mechanical properties of copper-ABS composite for FDM feedstock. *International Journal of Engineering Research and Applications* 3 (3), 1257–1263.

The Effect of In-Situ-Formed Silver Nanoparticles on the Morphological Properties of Epoxy Resin Filled Composites

MA Salim, R Hamidi, and AM Saad, Technical University of Malaysia Melaka, Durian Tunggal, Melaka, Malaysia

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Mohd A. Salim, Roshidah Hamidi, Adzni Md. Saad, The Effect of In-Situ-Formed Silver Nanoparticles on the Morphological Properties of Epoxy Resin Filled Composites, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2019, doi:10.1016/B978-0-12-803581-8.11359-1.

Introduction

Conductive ink is a special type of ink, which allows electric current to flow through it. The ink can be printed directly on a substrate or any flexible surface through a regular printing process. There are several varieties of conductive ink in the market and it is crucial to choose the suitable ink for any electronic application. The ink is usually applied to the substrate and slightly heated to evaporate the solvent and heat up the conductive particles together. Conductive ink is a significant component of any application, with extensively uses in photovoltaic cells, medical devices, membrane switches, as well as RFID chips. It is regarded as the next generation of an electronic device (Mohklis *et al.*, 2018).

Besides that, conductive ink, which is an ink printed to conduct electricity have been in some talk for a few years for their applications in printed electronics (PE) and flexible electronics (FE), respectively. It has the ability to print circuits on paper or some form of flexible surface through the inkjet printing technology. Although the early growth of the printed electronics industry is not as drastic as expected, there are some great demands to use these products (conductive inks) in daily activities such as cell phones, displays, smart wearable, lighting, small packaging, labels, shipping, storage and many more (Hamidi *et al.*, 2018). Conductive ink has been widely studied due to its popularity in printed electronic and demand from the market.

The process of choosing the right ink loading is a crucial successful factor for quick, simple and affordable production of PE prototypes and electronically functional prints. It is mainly based on the electrical properties of the conductive ink itself. In this experiment, the investigation in the characterization of conductive ink is related to the formulation of ink loading and preparation method of the ink samples (Lee and Oh, 2010).

Conductive ink is an innovation through research that had been conducted, which able to reduce cost and accelerate the fabrication of electronic components (Zheng *et al.*, 2013). There are many advantage of this technology such as its capability to print a controlled amount of ink at high frequency and on almost any type of substrate, low cost, additive and efficient handling of expensive materials. The materials of conductive filler vary in shapes and sizes, which consist of metal properties such as carbon (C), copper (C), gold (Au), and silver (Ag) particles (Mohklis *et al.*, 2018; Kamel *et al.*, 2018). There are many types of stretchable substrate that can be used in conductive ink like glass slide substrate, polyethylene terephthalate (PET), thermoplastic poly urethanes (TPU), polyurethane (PUT), and poly dimethyl siloxane (PDMS). Basically, these substrates do not tend to be very smooth and have a very low glass transitions temperature (T_g). Therefore, the temperature during curing process is generally under 150°. Another challenge regarding the ink substrate is the compatibility issue, which can cause metal delamination under mechanical and thermal stresses. These stretchable substrate tends to be quite thin (1–5 mils thick), hence they are easily stretched. Therefore, it can easily deform when the printing process takes place and leads to distortion in the printed image (Mohklis *et al.*, 2018).

In this article, it elaborates the effect of in-situ formed silver nanoparticles on the morphological properties of epoxy resin filled composites, which may become a future reference on macrostructure technology development.

Results and Discussion on Morphological Analysis

Ink Formulation

For the formulation of conductive ink in this experiment, the materials used are shown in Table 1. The material composition with various percentages is tabulated in Table 2.

The material composition starts from the least percentage of filler until the highest percentage of filler. The loading of hardener is 30% of the amount of binder loading. Total value from the table is the sum of filler loading and binder loading amount and it was set before the formulation process started, which is 2 g.

In-Situ Experimental Setup

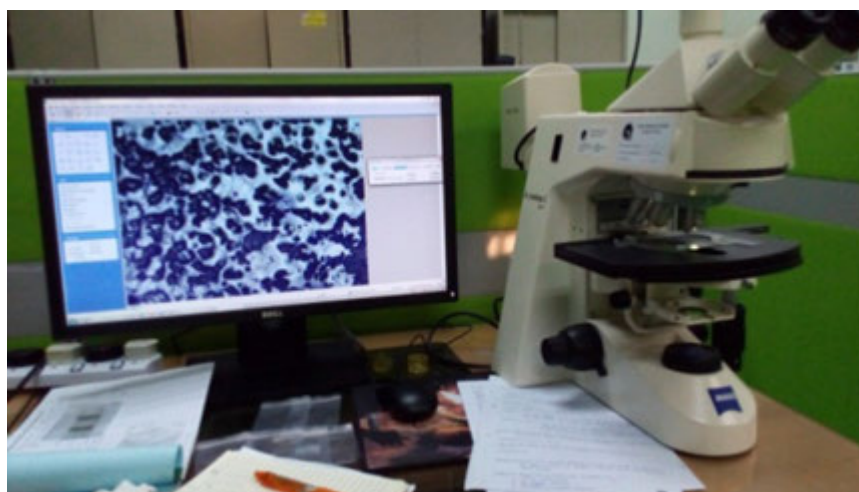
In Lu (2013) defined the microscopy as a method that provides the measurements of particle shape and size, morphology and the dispositions of nanoparticles by producing two-dimensional pictures of three-dimensional items. Fig. 1 shows the setup for in-situ morphological analysis.

Table 1 Materials used in ink formulation

Materials		
Silver nanoparticles (AgNPs)	Epoxy	Hardener
		
Used as the filler element	Used as the binder element, to bind the particles together	Used to harden or dry the mixture

Table 2 Composition of ink loading

Sample	Filler		Binder		Hardener (g)	Total (g)
	(%)	(g)	(%)	(g)		
1	10	0.2	90	1.8	0.54	2
2	20	0.4	80	1.6	0.48	2
3	30	0.6	70	1.4	0.42	2
4	40	0.8	60	1.2	0.36	2
5	50	1.0	50	1.0	0.30	2
6	60	1.2	40	0.8	0.24	2
7	70	1.4	30	0.6	0.18	2
8	80	1.6	20	0.4	0.12	2
9	90	1.8	10	0.2	0.60	2


Fig. 1 Setup for in-situ morphological analysis.

The microscope used in this experiment was connected to the computer so that the images from the microscope could be directly displayed on the screen. The sample was placed on the stage and it was held by the stage clips as can be seen in [Fig. 2\(a\)](#). The revolving turret was turned in order to secure the position of the required power objective lens. In this experiment, three power objective lens were used, which were 5x, 10x and 20x. Next, the focus knob was turned to move the stage upward or downward

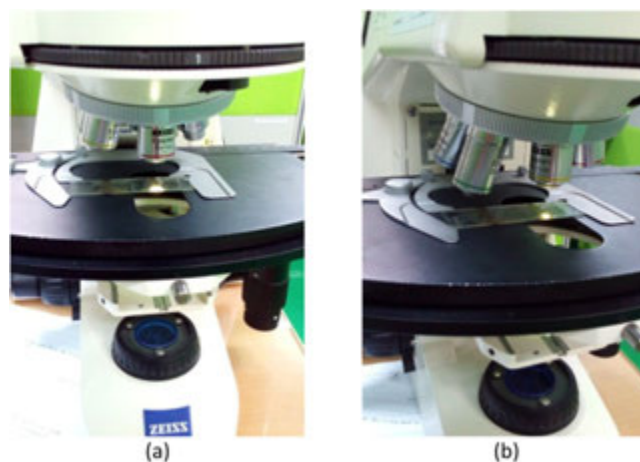


Fig. 2 (a) Sample was held by stage clips and (b) Light was directed to the position.

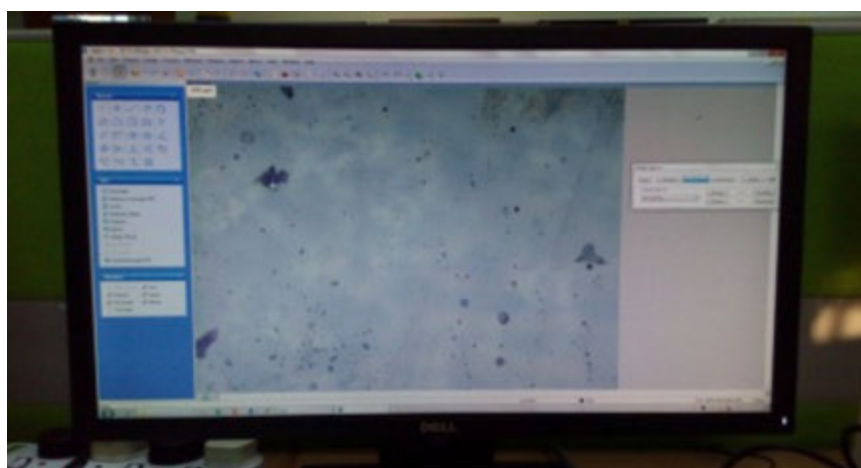


Fig. 3 Sample of morphological analysis for silver nanoparticles conductive ink.

without having the objective lens in contact with the sample until the light was directed to the desired position as shown in **Fig. 2 (b)**. The focus knob was turned until the image had been into focus mode.

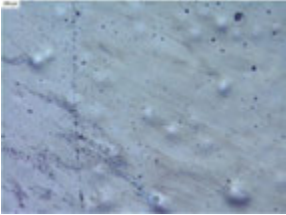
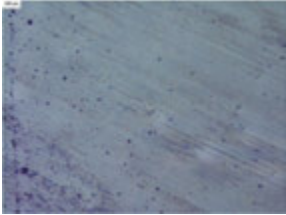
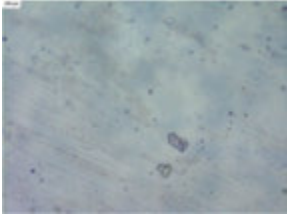
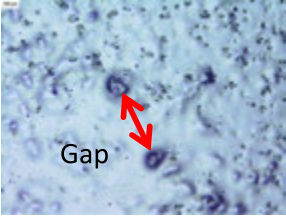
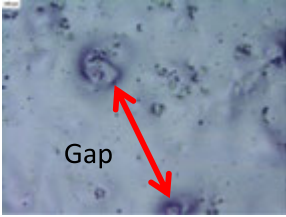
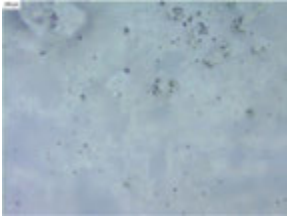
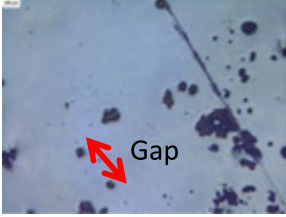
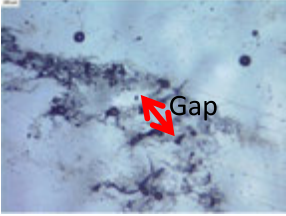
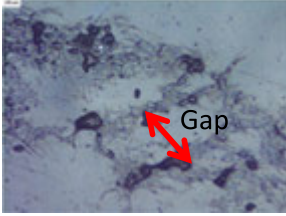
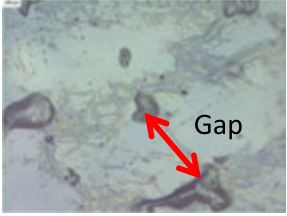
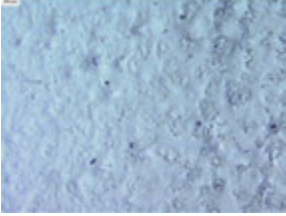
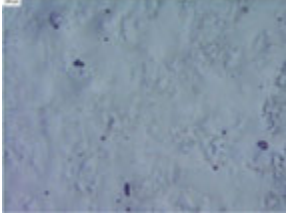
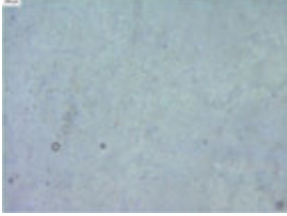
After a clear image of the sample was obtained, the image was recorded in the computer and the scale of the image was set up at 100 μm . Those described steps were repeated for another power objective lens as at each point; three images with different resolutions (5x, 10x and 20x) were required in this experiment. **Fig. 3** shows the sample of morphological analysis for silver nanoparticles conductive ink.

Morphological Setup

Light microscopy was conducted on the sample ink tracks to investigate the ink track in a microscopic condition. In this section, all of the microstructure images were divided into three categories, which were microstructure with no conductivity, microstructure that should have conductivity and microstructure with conductivity. The microstructure images were organized in accordance to their filler loading with three scales of magnification; 5x, 10x and 20x.

Table 3 discusses about the microstructural transformation of silver nanoparticles ink based on the filler loading in the range of 10% until 50%. For 10% of filler loading, the microstructure shows no appearance of silver nanoparticles element due to lack of filler loading as compared to the amount of binder and hardener. The binder and hardener conquer all over the ink track and if the conductor materials are low in quantity (Nash *et al.*, 2015), there is no conductivity at all. In overall, the 10% of filler loading only creates the formation of voids. While at 20%, 30% and 40% show the existence of gaps between silver nanoparticles. The frequency of gaps between silver nanoparticles can affect the electrical properties of the conductive ink layer as the increasing number of gap causes the resistance to increase. High voltage is required to ensure there is flow of current among the silver nanoparticles (Kazani *et al.*, 2012). Next, percentage of filler loading of 50% shows the presence of silver nanoparticles but in a very small quantity, which may be due to the same ratio of filler to binder.

Table 3 Microstructure with no conductivity at filler loading of 10%–50%

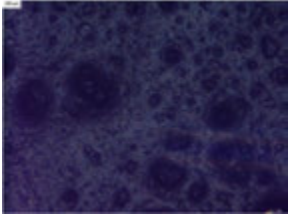
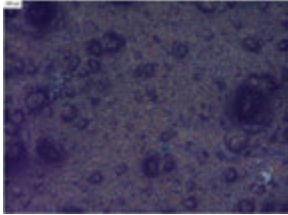
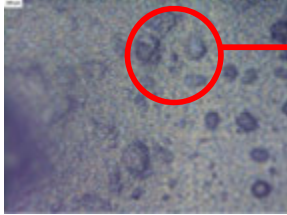
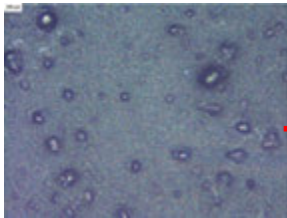
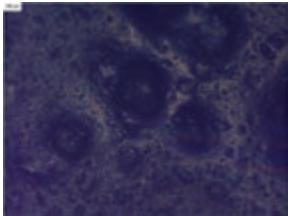
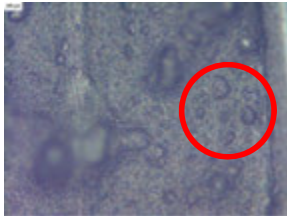
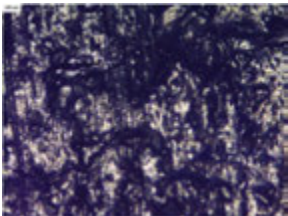
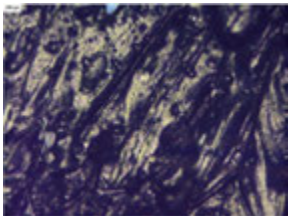
Filler (%)	Magnifications		
	5 ×	10 ×	20 ×
10			
20			
30			
40			
50			

Then, **Table 4** shows the filler loading that has contributed to the conductivity of the ink. The percentage of filler loading are from 60% to 80%. They display no outstanding difference between each other either in the shape of particle or size as compared to the filler loading at 90%. At 60% and 80%, the ink layer has the presence of granular-like particle. In order to be a conductive ink, the granular particle must contain a 3D connection of conduction, which leads to the existence of particle necking as discovered by researchers in 2005 (Kim and Moon, 2005).

Kim and Moon also believed that the necking growth provides a continuous connection and once the interparticle neck has been produced, the granular-like particle will be conductive although it is still porous. However, at first the 70% of filler loading does not show any traces of conductivity although it is expected to have the existence of conductivity in the ink layer. Based on the microstructure images, there have been some traces of scratch developed in the ink layer, which may be due to some mistakes happened during the printing process as it was manually deposited onto the substrate. After multiple times of fabricating the ink with 70% filler loading, finally the trace of resistivity within the ink can be identified with try and error process.

At 90% of filler loading, the dark color in the microstructure represents the presence of silver while the brighter region is the binder. Once it has already been melted, major changes can be noticed as most barriers between particles are vanished as discovered by researchers in 2011 (Kamyshny *et al.*, 2011). This indicates that the ink layers have a close-packed structure where

Table 4 Microstructure with conductivity of filler loading from 60% to 80%

Filler (%)	Magnifications		
	5 ×	10 ×	20 ×
60			 Granular particles
70	 Scratch lines		
80			
90			 Continuous particles

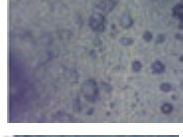
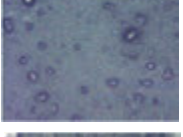
the particles create a strong bond between each other. Once the silver nanoparticles are in contact with each other, the particles become more continuous rather than being in the shape of discrete and spherical, thus the contact area between particles becomes bigger. Roberson explained that the increase of conductivity can be discussed only by the size of contact area through the percolation theory (Roberson *et al.*, 2011). In 2017, Jiang believed that the percolation theory can explain the situation of potentially the percolation can happen between each other when electricity flows through the structure of silver nanoparticles. The probability is based on the sintering process, where the probability is very low. The best percentage can also be achieved and this percentage is known as the percolation threshold (Jiang, 2017).

Relationship Between Rate of Resistivity, Surface Roughness and Morphological Analysis

Table 5 exhibits three parameters of each composition of sample, which are total average values of resistivity, total average values of resistivity and microstructure in order to construct a study of the relationship between sample composition and those three parameters.

For 10% until 50% of filler loading, there is no resistivity value that can be detected by four-point probe because the filler composition is low. Material of the filler is silver nanoparticles, which is widely known as conductor. So if the amount is low, it is possible that there is no resistivity that can be traced. Furthermore, the total average values of surface roughness are in the range of 0.1–1.2 μm and the total average values of surface roughness between horizontal and vertical direction show small difference. The difference indicates that the spreading of ink makes the surface to have stable consistency of irregularities. On top of that, the ink

Table 5 Comparison between rate of resistivity, surface roughness and morphological analysis

Filler (%)	Binder (%)	Point	Resistivity (Ω/sq)	Surface roughness (μm)		Microstructure (Magnification of $20\times$)	
			Total Average at Positions A & B	Total average at positions A & B			
				Horizontal direction	Vertical direction		
10	90	1	–	0.215	0.281	Dark spot is presumed as AgNPs	
		2	0.228	0.276			
		3	0.121	0.114			
20	80	1	–	0.943	0.689	Dark spot is presumed as AgNPs	
		2	1.507	0.229			
		3	1.135	0.111			
30	70	1	–	0.952	0.686	Dark spot is presumed as AgNPs	
		2	1.506	1.033			
		3	1.116	1.097			
40	60	1	–	0.469	0.561	Dark spot is presumed as AgNPs	
		2	0.228	0.364			
		3	0.340	0.300			
50	50	1	–	0.502	0.245	No obvious color difference due to the same amount between filler and binder	
		2	0.439	0.240			
		3	1.071	0.383			
60	40	1	136.148	4.238	4.264	Darker color due to filler amount is higher than binder amount	
		2	175.222	3.546	4.006		
		3	468.895	3.186	2.319		
70	30	1	40.555	3.516	4.434	Darker color due to filler amount is higher than binder amount	
		2	32.080	4.393	3.736		
		3	38.203	4.132	3.257		
80	20	1	6.277	4.335	4.299	Darker color due to filler amount is higher than binder amount	
		2	5.682	3.366	3.461		
		3	12.927	3.740	2.169		
90	10	1	0.143	4.765	5.721	Obvious colour difference that indicates filler and binder	
		2	0.100	5.279	5.890		
		3	0.085	5.641	5.716		

can be distributed evenly is contributed by the texture of sample that is less concentrated. For low viscosity ink, the printing activity becomes easier to carry out.

Apart from that, the sample texture that has low viscosity relates to the composition between the elements in the sample, which is the ratio of binder and hardener is higher than the ratio of filler. By having more binder and hardener in the sample, their microstructural behaviors are presumed to show brighter color of microstructure as they are in transparent form. Then, from 60% until 90% of filler loading, the resistivity of 60% of filler loading can be detected to have the highest total average value of

resistivity, which is 468.895 Ω/sq and the lowest is 0.1 Ω/sq from 90% of filler loading. The 90% of filler loading has the highest value of conductivity as the resistivity varies inversely with the conductivity value.

Moreover, the total average values of surface roughness are in the range of 2–5.9 μm . The highest value is 5.890 μm resulting from 90% of filler loading and the lowest value is 2.169 μm resulting from 80% of filler loading, which both are in vertical direction. With the high total average value of surface roughness, it can be presumed that the ratio of filler is higher than the ratio of binder and hardener. In addition, the filler is in the form of silver flake, which strongly makes the assumption acceptable.

For the sample with high composition of filler, its texture has high viscosity and it becomes more concentrated. Thus, during printing process, it requires extra work than usual in enabling the ink to cover the substrate evenly, which contributes to the rougher surface. Aside from having rougher surface, more filler in the sample is assumed to generate dotted spot or darker region in the microstructure as the silver nanoparticles are in dark or black color. In addition, noticeable difference of composition between filler and binder plus hardener can be presumed to be attributed by the obvious color difference in microstructure; brighter region versus dark region as displayed in 90% of filler loading.

All the results indicate that the samples with higher filler percentage has lower resistivity value and high value of surface roughness and vice versa. As for the microstructure, it is required to make the analysis for those two parameters; resistivity and surface roughness in order to find the best print resolution for optimizing the performance of printed electronics.

Conclusion

Based on the rate of conductivity for silver nanoparticles, it can be concluded that filler loadings of 10%, 20%, 30%, 40% and 50% do not have any presence of conductivity, while filler of loadings of 60%, 70%, 80% and 90% display the presence of conductivity. Thus, the decision to choose the best filler loading is merely based on the filler of loadings of 60%, 70%, 80% and 90% only. Moreover, filler loadings in the range of 60% until 90% show stable adhesion to the substrate. For the surface roughness, the lower filler loading produces smooth surface and higher filler loading shows surface irregularities. Finally, morphological analysis supports the results for both, rate of resistivity and surface roughness.

References

- Hamidi, R., Salim, M.A., Omar, G., April 2018. Sheet resistivity and morphological analysis of silver nanoparticles filled epoxy conductive ink. In: Proceedings of the 1st Colloquium Paper: Advanced Materials and Mechanical Engineering Research (CAMMER'18). Penerbit Universiti, Universiti Teknikal Malaysia Melaka, vol. 1, p. 4.
- Jiang, S., 2017. Inkjet Printing of Nano-Silver Conductive Ink on PET Substrate.
- Kamel, N.M., Salim, M.A., Omar, G. April 2018. Measurement of sheet resistivity on silver nanoparticles-filled epoxy conductive ink using thermoplastic polyurethane. In: Proceedings of the 1st Colloquium Paper: Advanced Materials and Mechanical Engineering Research (CAMMER'18). Penerbit Universiti, Universiti Teknikal Malaysia Melaka, vol. 1, p. 5.
- Kamyshny, A., Steinke, J., Magdassi, S., 2011. Metal-based inkjet inks for printed electronics. *The Open Applied Physics Journal* 4 (1),
- Kazani, I., Hertleer, C., De Mey, G., *et al.*, 2012. Electrical conductive textiles obtained by screen printing. *Fibres & Textiles in Eastern Europe* 20 (1), 57–63.
- Kim, D., Moon, J., 2005. Highly conductive ink jet printed films of nanosilver particles for printable electronics. *Electrochemical and Solid-State Letters* 8 (11), J30–J33.
- Lee, D.J., Oh, J.H., 2010. Inkjet printing of conductive Ag lines and their electrical and mechanical characterization. *Thin Solid Films* 518 (22), 6352–6356.
- Lu, K., 2013. *Nanoparticulate Materials: Synthesis, Characterization, and Processing*. Hoboken, NJ: Wiley.
- Mohklis, M., Salim, M.A., Masripan, N.A., Md. Saad, A., Omar, G., 2018. Nano indentation studies on graphene nanoparticles reinforced epoxy resin as conductive ink. *International Journal of Advanced Materials Characterization* 1 (1), 8–11.
- Nash, C., Spiesschaert, Y., Amarandei, G., *et al.*, 2015. A comparative study on the conductive properties of coated and printed silver layers on a paper substrate. *Journal of Electronic Materials* 44 (1), 497.
- Roberson, D.A., Wicker, R.B., Murr, L.E., Church, K., MacDonald, E., 2011. Microstructural and process characterization of conductive traces printed from Ag particulate inks. *Materials* 4 (6), 963–979.
- Zheng, G., Cui, Y., Karabulut, E., *et al.*, 2013. Nanostructured paper for flexible energy and electronic devices. *MRS Bulletin* 38 (4), 320–325.

Toughening Mechanisms of Devulcanized Rubber Modified Epoxy Based Composites Reinforced With Zirconia

Alaeddin B Irez, CentraleSupélec, University Paris-Saclay, Gif-sur-Yvette, France and University Paris-Saclay, Gif-sur-Yvette, France
Emin Bayraktar, Supmeca-Paris, School of Mechanical and Manufacturing Engineering, Saint-Ouen, France
Ibrahim Miskioglu, Michigan Technological University ME-EM Department, Houghton, MI, United States

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Alaeddin B. Irez, Emin Bayraktar, Ibrahim Miskioglu, Toughening Mechanisms of Devulcanized Rubber Modified Epoxy Based Composites Reinforced With Zirconia, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2018, doi:[10.1016/B978-0-12-803581-8.11329-3](https://doi.org/10.1016/B978-0-12-803581-8.11329-3).

Introduction

In our day, environmental and economic concerns steered material manufacturers to produce new robust, lightweight and eco-friendly materials. Because, mass reduction by using lightweight materials decreases the fuel consumption of the vehicles which brings low CO₂ emission and low operating costs in return. In this regard, aeronautic and automobile industries work on the substitution of metallic components by composite materials. At this point, multifunctional composite materials can respond the expectations of the industry.

Polymer based composite materials can have high specific strength with the contribution of resistant fillers. In this context, epoxy is a thermoset polymer which is widely used in many different applications due to its favourable properties such as decent chemical resistance and ease in modification versatility as well as its inherent low viscosity and volatility [1]. However, epoxies generally reinforced with different reinforcements to meet the expectations. The modification of epoxy resins is generally done in different modes. First, the addition of hard particles such as glass beads or ceramics [2]. In the literature, the examples of using metal oxides such as TiO₂ and Al₂O₃ are widely seen. Nevertheless, few scientific information is available for epoxy-zirconium dioxide (zirconia) composites. Zirconia has superior properties such as high fracture toughness, high strength, outstanding wear resistance, high hardness and excellent chemical resistance [3–6]. Therefore, zirconia particles may serve as an appealing option to be used as reinforcement of epoxy to possess high tribological and mechanical properties.

Second type of modification is seen as the inclusion of thermoplastics or by the addition of elastomeric materials. Highly-crosslinked epoxy resin exhibits high brittleness because of the restriction of the plastic deformation and it has poor resistance to crack initiation and growth. Modifiers less rigid than the matrix can serve as unique toughness developers by enhancing the ductility [7]. The formation of the micro voids thanks to the rubber addition activates yielding processes because of the reduction of the local yield stress. Therefore, a significant amount of energy is dissipated within the plastic zone near the crack tip [8]. In particular, fresh scrap rubber enrich this study in terms of environmental and economic perspectives. Because, non-used vulcanized scrap rubber causes to costly landfills. Besides, in the context of landfilling, because of the impermeability and shape of scrapped tires, they keep water for a long time and this creates a habitat for mosquito larvae as well as other animals such as snakes and rodents [9,10]. These may carry infections namely malaria, cephalitis, chikungunya and dengue. Also, if these piles catch fire, it is quite onerous to extinguish them [11]. Once for all, some additives of landfilled tires such as colorants, flame retardants, stabilizers and plasticizers may leach from the bulk of the tires to the soil. Therefore, they can harm or kill some beneficial bacterial colony in the soil [12]. In consequence, in this study we open a window into the green manufacturing of the multifunctional composites by recycling of vulcanized rubbers.

The present work represents processing of recycled rubbers treated with epoxy resin to create novel composites in economic way. Main objective of this research is to determine the mechanical and tribological properties of these composites by using recycled rubber and epoxy as a matrix reinforced with zirconia. During this study, physical properties such as glass transition temperature and phase transitions are determined with dynamical mechanical analysis (DMA) and differential scanning calorimeter (DSC). Then, bending tests are realized with smooth and single edge notched beam (SENB) specimens. After that, nano indentation tests are examined to see the time dependent behaviour and wear characteristics. In addition, surface hardness is determined by means of Shore D hardness measurement and tribological characteristics are evaluated after realization of different macro and micro test technics. At the end, fracture surfaces are observed by means of scanning electron microscopy (SEM) to study the toughening and damage mechanisms.

Experimental Conditions

Materials Processing

The use of recycled rubbers inside epoxy matrix is more complicated than general belief for several reasons. Due to the previously conducted vulcanization process, cross-linked structure of rubber restrains the movement of rubber chains and limit the interaction forces between scrap rubber particles and epoxy matrix. In consequence, a reduction in the performance of final product is observed [13–15]. In this case, to enhance materials properties of the final product, devulcanization operation is recommended. According to ASTM definition, devulcanization is “a combination of depolymerization, oxidation and increased plasticity” since

during reclamation each of these processes generally occurs. *In fact*, the reverse of the vulcanization can be named as devulcanization [16]. During sulphur vulcanization, C-S and S-S bonds are formed. On the other hand, in an ideal devulcanization process, it is anticipated only C-S and S-S bonds cleavage without any main-chain degradation. Devulcanization occurs if the provided energy is higher than the link energies of monosulfidic C-S (270 kJ/mol) and polysulfidic S-S (240 kJ/mol) bonds without exceeding that of peroxide C-C (345 kJ/mol) bonds. In the frame of the current work, the energy for devulcanization is provided by microwaves and it is followed by chemical surface treatments. This combined method consists exposing recycled rubbers to microwave heating in a short time pursued by a pre-chemical treatment that is applied in practical point of view. Thereby, a good cohesion is provided at the interface between epoxy resin and rubber powders to improve the properties of the recycled rubber (SBR with a particle size varying from 30 to 130 μm .) coming from the sportive equipment. It means that they are fresh, clean and completely different from ground tire.

A new design of epoxy-based composite, reinforced with fine scrap-rubber powders and 3% Yttrium stabilized ZrO_2 is prepared in several steps:

After drying of the chemical treated rubber powders, at the final stage, devulcanized rubbers are mixed with epoxy resin powders. This mixture is used as a matrix of the new composites then, the new designed composites are manufactured by using classical powder metallurgy methods. After the mixture of the reinforcements (ZrO_2) in the matrix, milling process is carried out during 4 h.

- (1) Recycled rubbers are exposed to short microwave heating during 4 min in order to avoid degradation of the main chains [17].
- (2) Chemical treatment is applied. The procedure of the chemical treatment consists in a short silanization process followed by acrylic acid and a small amount of toluene solution to activate the surface of the rubber particles [18].
- (3) After treatment, the mixture is dried in the oven to eliminate any trace of the treatment chemicals. The mixture of epoxy resin and rubber powder is then milled 2 h to obtain a homogenous compound then heated at 80°C for 2 h and this mixture is used as matrix.
- (4) Then, the rubber-epoxy and zirconia are combined in a blender and milled for 2 h.
- (5) After blending of matrix and reinforcements, the new designed composites are manufactured by using classical powder metallurgy methods. The specimens are then manufactured by hot compacting (double uniaxial action) under a pressure of 70 MPa at a temperature of 180°C for 30 min. All of the specimens (30–50 mm in diameter) are cooled slowly.
- (6) Lastly, specimens are post-treated isothermally at 80°C for 48 h.

This procedure is illustrated in Fig. 1.

The compositions of zirconia reinforced epoxy and recycled rubber-based composites (called as ERZY I-II-III hereafter) are given in Table 1.

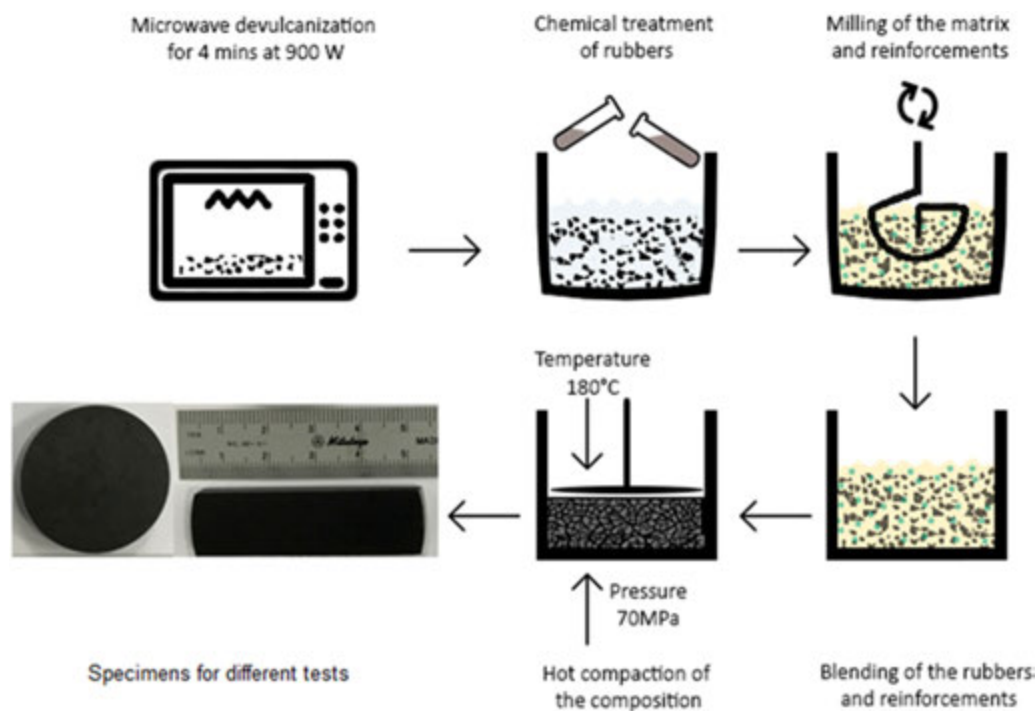


Fig. 1 Manufacturing of recycled rubber modified epoxy-based composites.

Table 1 Composition of the epoxy-rubber based composites

Epoxy-rubber based composition Epoxy – SBR rubber (10 phr)	ERZY I	ERZY II	ERZY III
Reinforcements (wt%)	2 ZrO ₂	4 ZrO ₂	6 ZrO ₂

Thermal Analyses and Physical Characterization

Dynamic properties, storage modulus (E') and mechanical loss angle tangent ($\tan \delta$) of the epoxy-based composites are investigated using a Dynamic Mechanical Thermal Analyser Q800 system (TA Instruments). The data are obtained at a frequency of 1 Hz, 0.1% strain in the temperature range from -80 to 200°C using a heating rate of $3^\circ\text{C}/\text{min}$ under single cantilever bending mode. The dimensions of the investigated samples are as follows: width 10 mm, length 30 mm, and the thickness 3 mm.

Differential scanning calorimeter (DSC) analyses are performed on DSC Q10N2 apparatus of TA Instruments, USA, from -80 to 400°C in air flow with a $1\text{ dm}^3/\text{min}$ flow rate and heating rate of $10^\circ\text{C}/\text{min}$.

Microstructure – Fracture Surface Analyses and Shore-D Hardness Measurements

Fracture surface damage analyses and microstructural observation have been realized by means of optical (OM) and scanning electron microscopy (SEM). SEM observation is realized on fracture surface of the tested specimens with Scope/JSM-6010LA Jeol® electron microscope.

Surface hardness measurements of the specimens are performed after post curing. Shore D hardness test measurements on the polished flat surfaces of the specimens are carried out according to ASTM D 2240 using Shore D hardness tester, (type HBD-100-0).

Fracture Toughness Measurements

There-point bending tests (3PB) have been carried out according to the ASTM D790 standards. Deflection of the specimen is measured by the crosshead position and crosshead speed is selected as $1\text{ mm}/\text{min}$. Flexural strength, strain and modulus are obtained from the test results. The test specimen is placed to the Instron 5569 bending test machine's supports and force is applied until it breaks. At least three specimens for each composition are used and standard deviation and average values are given in results article with standard deviation values.

In addition, fractural properties such as plain strain fracture toughness (K_{Ic}) and critical strain energy release rate (G_{Ic}) are investigated with single edge notched beam (SENB) specimens and the tests are realized according to ASTM D5045 standard. Notches are introduced by tapping a fresh razor blade.

Nano-Indentation Analyses by Means of Creep and Wear Tests

The time dependent behaviour is examined by means of a nano-indenter performing creep tests for three compositions manufactured to. A Berkovich indenter realized twenty indents on a 5×4 grid on each sample. The indents are spaced $50\text{ }\mu\text{m}$ along the 5-indent side and $75\text{ }\mu\text{m}$ along the 4-indent side. The load is increased at a rate of $1\text{ mN}/\text{s}$ to the max load and kept at the maximum load for 500 s then unloaded.

In addition, nano-indenter is utilized to perform relatively fast wear tests by forming scratch over the specimen. The damaged area after scratches is observed to compare the wear behaviour of the different samples. These nano wear tests are conducted by a conical tip with a 90° cone angle. Tests are run under a normal load of 20 mN applied over a linear track of 500 nm for 50 cycles.

Damage Analysis by Means of Scratch Test and 3D Optical Roughness Meter

In the current research basic idea on the tribological behaviour of the epoxy and recycled elastomer-based composites is evaluated performing scratch tests. A 3D optical surface scanner is utilized to assess damage zone after the scratch test in terms of scratch depth and average scratch roughness.

The contact between the sliding diamond indenter and the surface of the composite material during scratch test is analyzed. The normal and tangential forces on indenter are recorded. However, main focus is given to the damage area and volume. In the frame of the current research, the resistance to scratch deformation is evaluated in terms of scratch depth, surface and worn volume subsequent to scratching only under dry conditions and 50,000 and 100,000 number of cycles of wear.

Results and Discussions

Microstructure of the Composites and Hardness Measurement

In Fig. 2 two different specimens are shown in different diameters for different characterizations. They are manufactured by means of hot compaction technics.

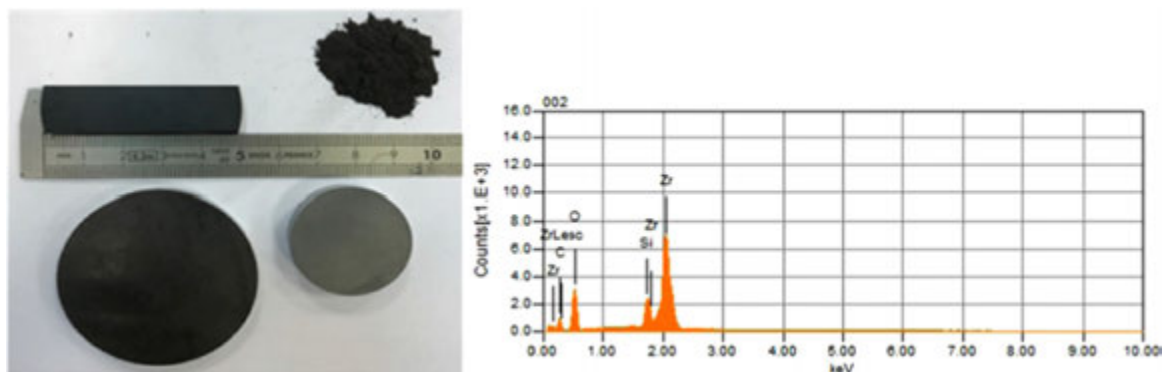


Fig. 2 Specimens with a diameter of $d = 30\text{--}50$ mm produced from the recycled rubber modified epoxy based composites reinforced with zirconium.

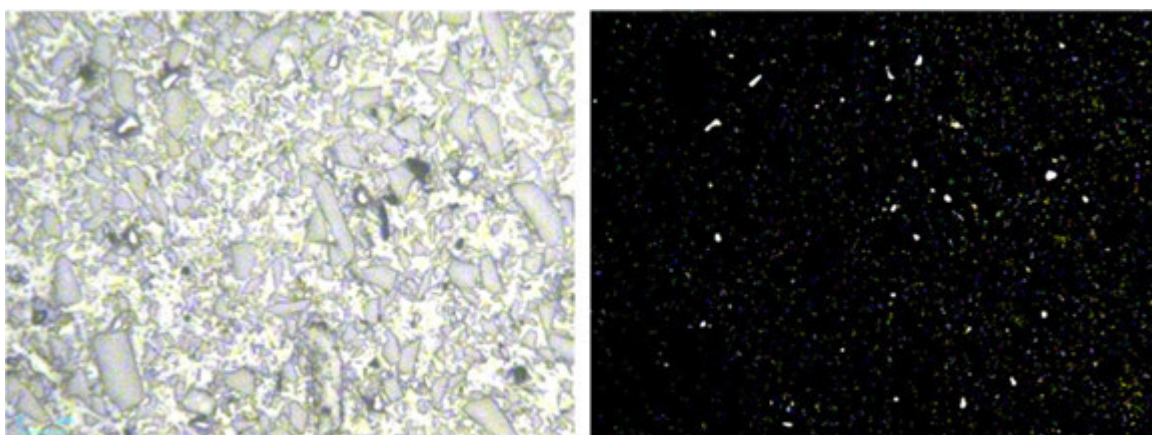


Fig. 3 Microstructure of ERZY I and BES with position of the reinforcements.

Table 2 Hardness values of ERZY specimens

<i>Hardness measurement</i>	
Specimen	Shore D
ERZY I	86
ERZY II	92
ERZY III	87

General microstructures of one of the compositions are shown in **Fig. 3**. All of the compositions have shown a considerably homogenous distribution of the reinforcements in the structure. Essentially, it is seen that the adhesion of the rubber to the epoxy matrix is very successfully carried out after the chemical treatment. In the figure, an amorphous particle is observed and it is considered as a rubber particle. In addition, light coloured homogeneously distributed particles are the inclusions of epoxy matrix. Also, the gap under 100 micron of the rubber particle is commented as an extracted rubber particle during polishing process.

After microstructure observations, Shore D hardness results are given in **Table 2**.

Thermal Analysis and Physical Characterization

After all milling and material preparation processes, DSC analysis are realized on unpolymerized powder compositions and the results are given in **Fig. 4**. It is seen that curing started slightly above the room temperature and it finished around 160°C . Also, it is commented that physical and/or chemical reactions occur intensely around 330°C which are commented as degradations over 300°C . Besides, the values determined from the area of exothermic peak at a particular temperature did not vary considerably upon the addition of zirconia indicating that the presence of fillers has not affected remarkably the reaction enthalpies.

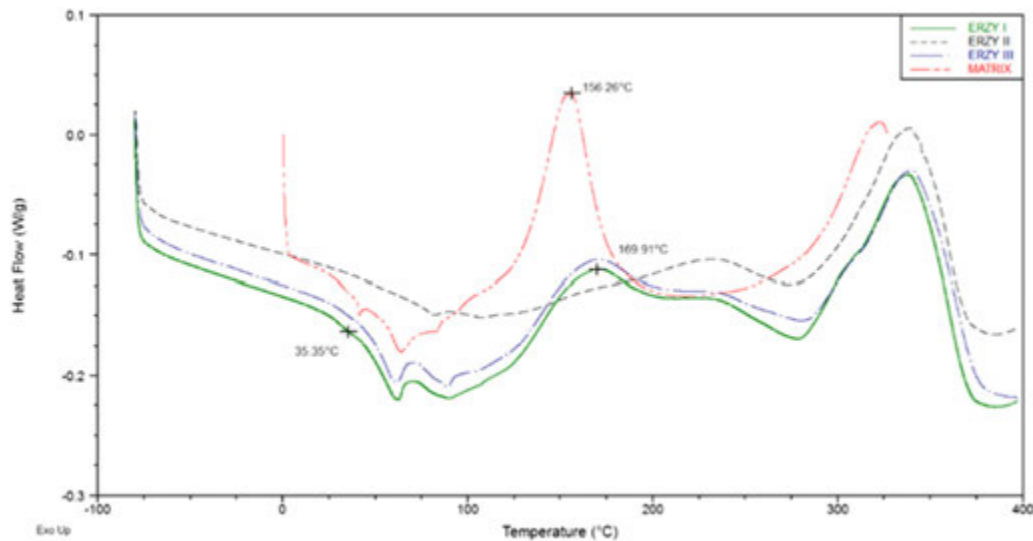


Fig. 4 DSC analysis results of ERZY specimens: Evolution of heat flow as a function of temperature.

After DSC analyses, elastic response and viscous response of the material are evaluated by determining respectively storage modulus (E') and loss modulus (E'') under dynamic loading. Then, the loss factor ($\tan \delta$) is determined by taking the proportion of loss modulus to storage modulus which is a measure of the energy lost from the material under loading at different temperatures. It shows the internal friction or mechanical damping in a viscoelastic material [19]. After acquiring the results, T_g can be determined by taking the first inflection point, or the onset of the drop-in storage modulus. Nevertheless, the simplest approach to determine T_g is taking the peak of $\tan \delta$ [20].

Fig. 5 exhibits the $\tan \delta$ and storage modulus at different temperatures for different compositions. T_g of these composites are determined around 125°C and it is seen that there is a monotonic increase T_g trend with the increasing zirconia content. Hence, it can be said that increasing amount of zirconia particles hinders the segmental polymer chain mobility. In addition, the increase in zirconia content showed a decrease in the $\tan \delta$ peak. This decrease in $\tan \delta$ indicates higher adhesion between fibers as alleged from E' curves. Because, better fiber-matrix adhesion results in low damping in the composites. Due to the fact that, after T_g these composites have quite low mechanical resistance, DMA analysis is important to determine T_g which should be considered during design process.

Three Point Bending Tests and Fracture Surface Observation

Three-Point Bending (3PB) tests have been carried out for each different type of composites.

Flexural stress is calculated during three-point bending test according to the Eq. [1]:

$$\sigma = \frac{3Pl}{2bh^2} \quad (1)$$

In this formula, l is the span length, P is the maximal bending load, b and h are the sample thickness and depth, respectively. Flexural strain, ε_f , is determined according to the Eq. [2]:

$$\varepsilon_f = \frac{6Dh}{l^2} \quad (2)$$

D is the maximum deflection at the center of the specimen.

E_B is the modulus of elasticity in bending and it is expressed with the Eq. [3] as follows;

$$E_B = \frac{l^3 m}{4bd^3} \quad (3)$$

m is the tangent of the initial straight portion of the stress-strain curve.

The mode I fracture toughness, K_{Ic} , is determined by testing of the single edge notched beam (SENB) specimens and K_{Ic} is calculated according to the Eq. [4]:

$$K_{Ic} = \frac{F}{Bw^{1/2}} f(x); x = \frac{a}{W}, 0 < \frac{a}{W} < 1 \quad (4)$$

F is the maximum force from the load-elongation trace; B is the thickness of the specimen; W is the width and " a " is the total notch length.

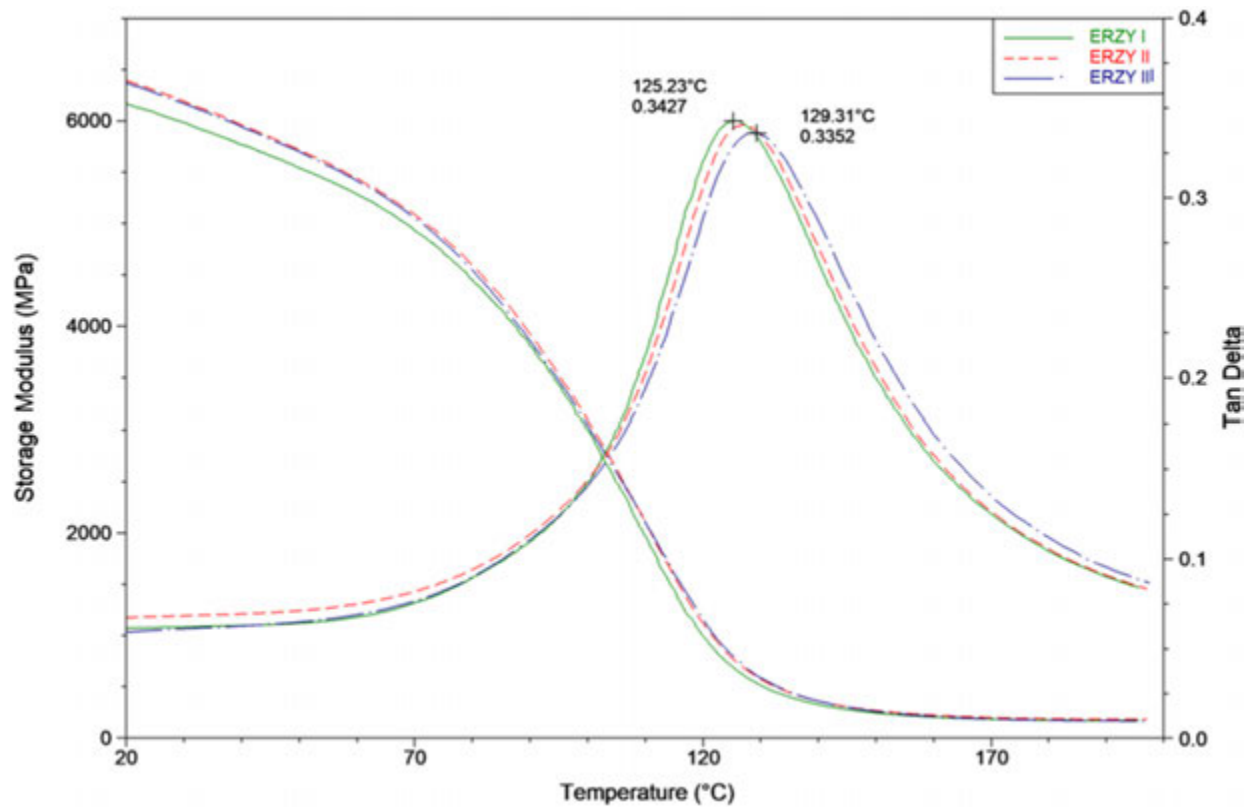


Fig. 5 Evolution of storage modulus and tan δ as a function of the temperature for three ERZY specimens.

Table 3 Comparison of mechanical properties of ERZY specimens

Composition name	ZrO ₂ (wt%)	Ultimate flexural stress (MPa)	Flexural modulus (GPa)	Strain at break ($\epsilon\%$)	K_{Ic} (MPa m ^{1/2})	G_{Ic} (kJ/m ²)
Matrix	–	42,13 $\pm$ 6,05	7,88 $\pm$ 0,79	0,66 $\pm$ 0,07	1,44 $\pm$ 0,12	0,66 $\pm$ 0,11
ERZY I	2	33,15 $\pm$ 3,26	3,76 $\pm$ 0,78	0,96 $\pm$ 0,06	2,45 $\pm$ 0,32	1,62 $\pm$ 0,15
ERZY II	4	32,04 $\pm$ 2,87	4,32 $\pm$ 0,63	0,92 $\pm$ 0,04	2,23 $\pm$ 0,18	1,23 $\pm$ 0,10
ERZY III	6	24,27 $\pm$ 4,13	3,96 $\pm$ 0,82	0,65 $\pm$ 0,04	1,97 $\pm$ 0,27	1,07 $\pm$ 0,13

$f(x)$ is the geometry correction factor and is expressed with the Eq. [5] as follows;

$$f(x) = 6(x)^{0.5} \left\{ \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{1.5}} \right\} \quad (5)$$

Critical strain energy release rate (fracture energy) G_{Ic} is calculated using the expression Eq. [6] as:

$$G_{Ic} = \frac{K_{Ic}^2}{E} (\text{plane stress}) \quad (6)$$

where E is the elasticity modulus for plane stress approach examined for thin specimens.

In Table 3 flexural stress, modulus and strain values are given. From the table it is observed flexural strain is enhanced by the zirconia reinforcement. As seen in DMA analysis, loss moduli of the composites are increased. This signifies that viscoelastic characteristic of the composites is improved. Therefore, flexibility of the composites enhanced while the flexural stress and moduli reduced. The main reason for this situation is considered as the quite hard nature of the zirconia. Because, by the increase in their mass rate, they create clusters and they tend to behave as crack nucleation sites upon loading [21]. Even if they can be robust enough to improve the flexural modulus, they constitute weak points, that leads to failure when the stress is applied [6].

Fracture toughness is also examined and the results indicate an improvement in the stress intensity factor as well as fracture energy. However, fracture toughness and energy showed a downward trend by the rise in the zirconia content. This may originate because of the excessive amount of very hard particles which behaves as stress concentrators.

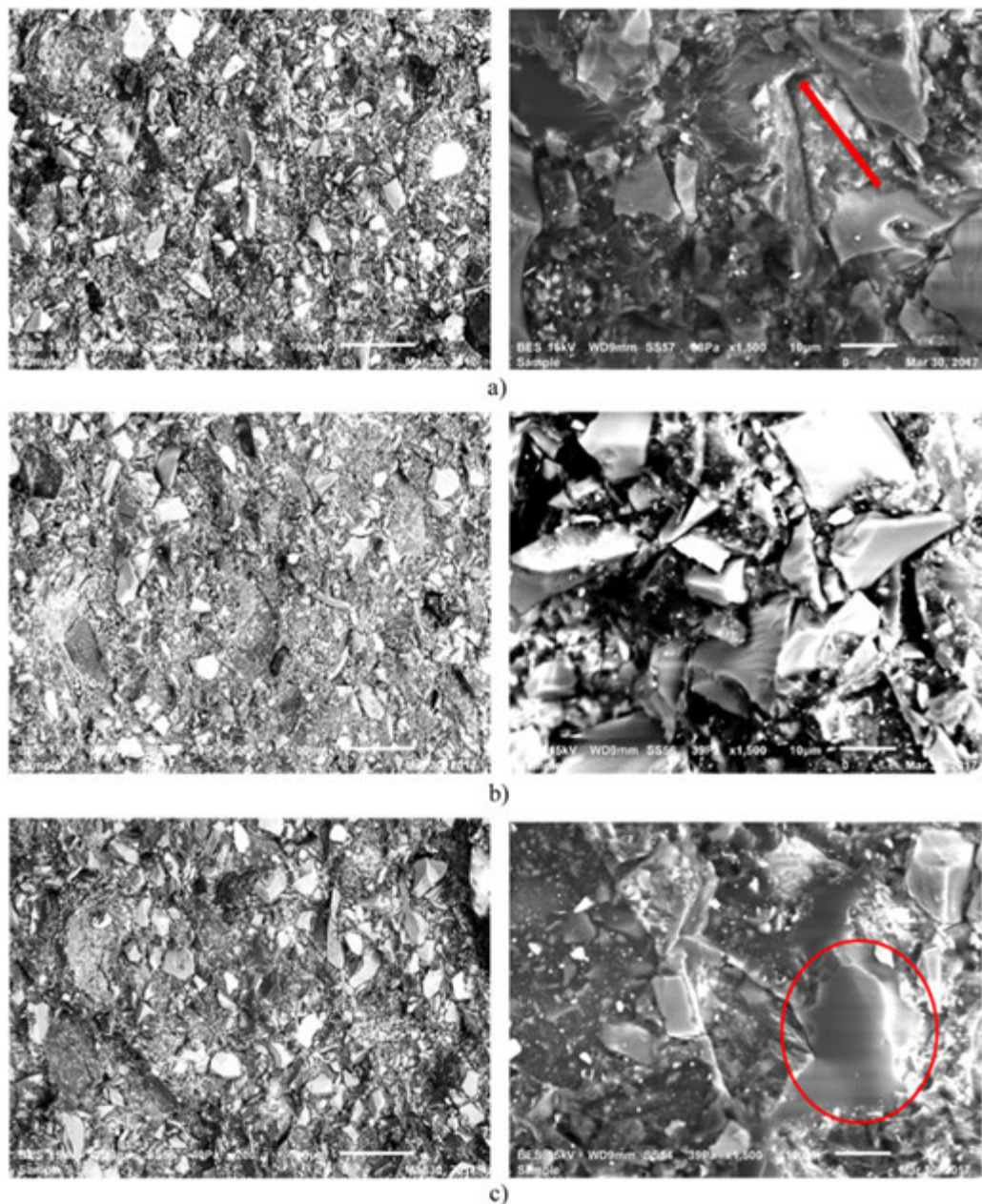


Fig. 6 Fracture surfaces after 3PB testing (a) ERZY I (b) ERZY II (c) ERZY III.

SEM observation is carried out on fracture surfaces after flexural tests. **Fig. 6** shows the fracture surfaces of ERZY I-II-III composites in different magnifications. As first impression, zirconia particles are homogeneously distributed over the matrix. Also, debonding of the reinforcements is not observed remarkably. This signifies the good adhesion of matrix and reinforcements. Also, rough fracture surfaces support this statement. In addition, existence of hard fillers brings with crack pinning toughening mechanism in these composites as seen in the **Fig. 6(a)** inside the red circle. Crack propagation continued until confronts a hard particle than it is stopped. Last but not least, in **Fig. 6(c)** plasticized matrix justifies the improvement in the viscoelastic behaviour.

Time Dependent Behaviour by Means of Nano-Indentation

Collected data during each indentation is used to calculate the creep compliance and the stress exponent defined in Eq. [7] [22]:

$$\varepsilon(t) = \sigma_0 J(t) \quad (7)$$

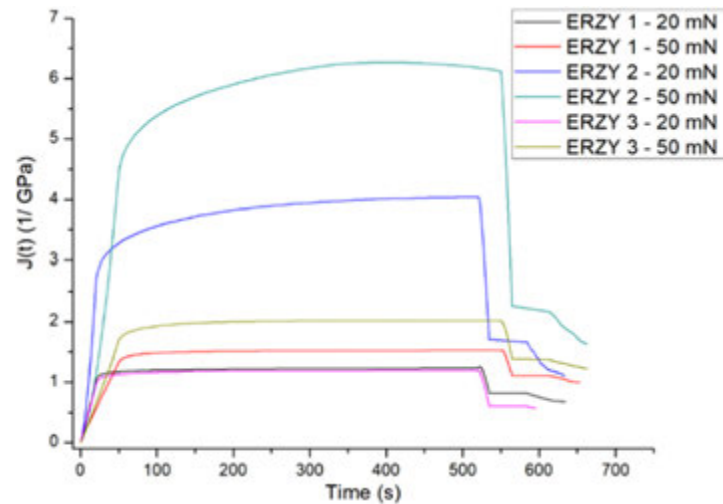


Fig. 7 Creep Compliance curves for specimens ERZY I-II-III, under 20 mN and 50 mN load.

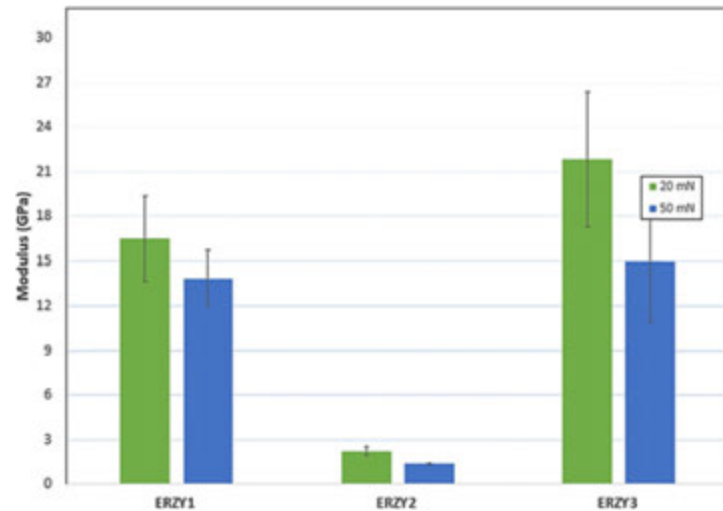


Fig. 8 Indentation modulus for the three composites under 20 mN and 50 mN.

where σ_0 is the constant stress applied and $J(t)$ is calculated using Eq. [8]:

$$J(t) = A(t) / (1 - (\nu)) P_0 \tan \theta \quad (8)$$

In Eq. [8] $A(t)$ is the contact area, P_0 constant applied load, θ is the effective cone angle which is 70.3° for a Berkovich indenter and the Poisson's ratio (ν) is assumed to be 0.3. This approach takes into account how the contact area under the Berkovich tip alters while displacement into the surface changes.

In Eq. [9] the strain rate is given. The strain versus time behaviour during creep is characterized by a high strain rate $\dot{\epsilon} = dc/dt$ in the primary stage of creep and then in the secondary, steady state stage of creep:

$$\dot{\epsilon} = K \sigma^n \quad (9)$$

where n is the stress exponent and K is a constant. The strain rate is calculated in the software and in turn n is obtained from the log-log plot of strain rate versus stress in the secondary stage of creep.

A large scatter in the data is observed due to heterogeneous nature of the materials under consideration. The nano-indentation test is carried out over a small area/volume, and the results from a small area can be misleading. In order to overcome this, sampling number is taken as large as possible then Fig. 6 is plotted from the average values.

According to Fig. 7 creep compliance is improving until a certain point of increasing rate of zirconia then it decreases. This signifies that, at the beginning zirconia improves the viscoelastic characteristic, following trend may show differences because of the inhomogeneities in the measurement zone [23].

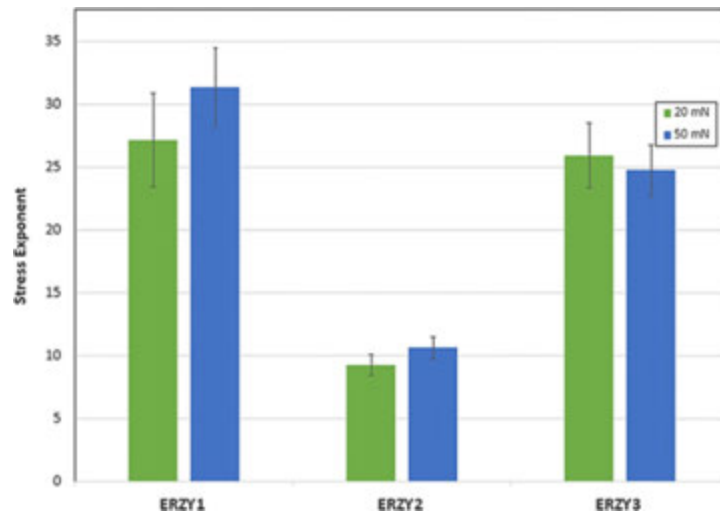


Fig. 9 Stress exponent for the three composites under 20 mN and 50 mN.

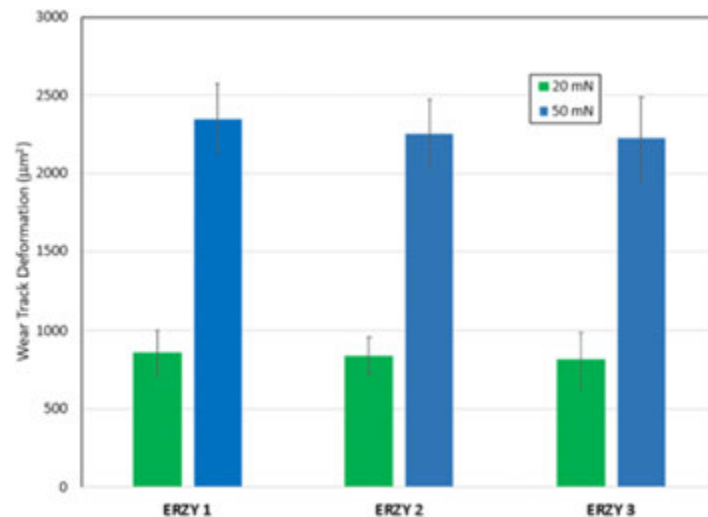


Fig. 10 Comparison of wear track deformation for ERZY composites.

Linear viscoelastic models can be applied to these materials to compare the results with nanoindentation. Nevertheless, these models do not consider the case of tip-specimen adhesion which may differ from experimental results.

In addition, the average indentation modulus and stress exponent values are obtained from the 20 indentations performed under 20 mN and 50 mN constant loads and they are presented in Figs. 8 and 9 with error bars showing $\pm$ one standard deviation.

First remarkable point on the Fig. 7 is thought as the wide interval of deviation values. This situation is commented as a consequence of indentation test. Because, test is performed over a very small area and when indenter tip comes across zirconia rich zone or a matrix rich area big differences are observed. Different researchers have indicated for polymers and polymer-based composites that modulus as determined by nano-indentation is higher than that determined by macroscopic tensile tests. This inequality is thought as a consequence of pile up of material around the contact impression and viscoelasticity of the polymer and polymer-based composites which are not taken into consideration during the modulus determination by the Oliver-Pharr method [24–26].

Fig. 8 indicates a similar tendency with the creep compliance values which verifies given equations.

Wear Testing by Nanoindentation

As the last step of nano-indentation technic, the indenter generated scratches over the specimen. These scratches give a practical idea regarding the wear resistance of material. One cycle is defined as a pass and return of the indenter over the track, so the total distance covered for one wear test is 0.050 m. Speed of the tip during wear tests is 50 $\mu\text{m/s}$. By examining the area of damaged

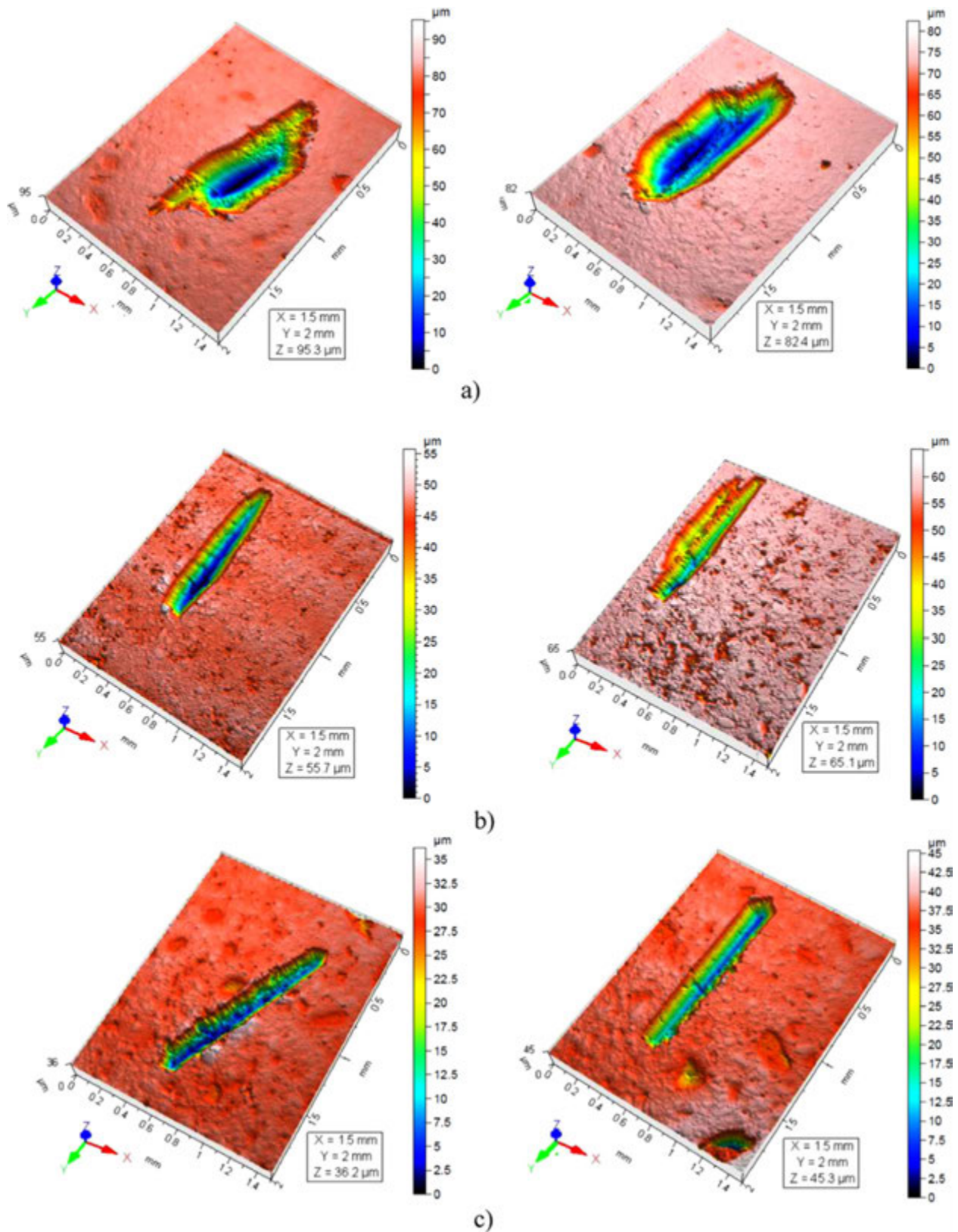


Fig. 11 Three dimensional damage traces obtained in the direction of width and length for the specimens ERZY I-II-III (respectively a,b,c) for 50 k (left) and 100 k cycles (right).

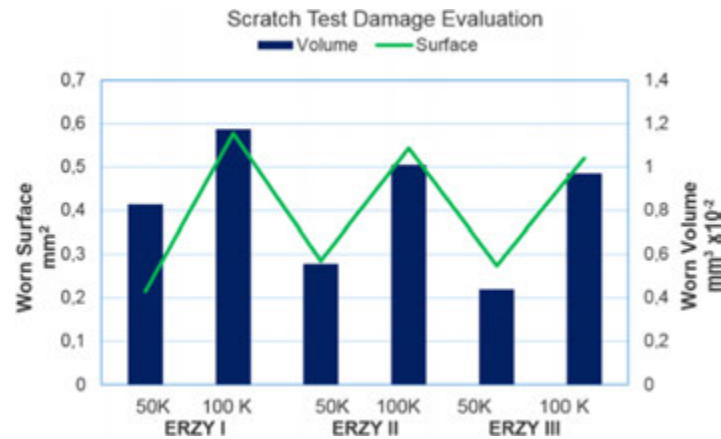


Fig. 12 Worn volume and surface subsequent to scratch tests.

Total of 10 wear tests for each specimen are performed under the two normal loads. The wear in a track is characterized as the worn area between the initial profile and the residual profile of the wear track.

Fig. 10 shows the average of the deformation on ten wear tracks. This is attributed to the inhomogeneity in the scratched zone. Also, a very small area is examined by nanoindentation technique. For this reason, macro scratch tests can present more reliable results. In this regard, macro scratch tests are performed.

Damage Analysis by Means of Scratch Test and 3D Optical Roughness Meter

As mentioned above macro scratch tests gives more explicit results. Here, after realizing three different group of macro scratch tests, a 3D optical surface scanner generated a cartography of the damaged zone. The results are presented in the **Fig. 11**.

In **Fig. 12** the surface of the damage trace after scratch calculated from roughness test results are given. There is a coherency in the results obtained from nano wear test. As expected, zirconia particles get the material more resistant to wear on the surface. This situation is supported by the worn volume values. Also, increased number of cycles did not contradict the previous statement.

The main reason for damage of the matrix and reinforced filler interfaces is thought as the high shear stress at the interfaces the interfacial shear stress. In addition, when the indenter is slipping, tangential tensile stress is caused on the surface behind the indenter, while in front of the indenter the tangential stress is compressive.

Conclusions

After manufacturing of epoxy-recycled rubber based composites, microstructure is observed with SEM. From the images, a homogeneous distribution of the reinforcements is observed. 3PB tests showed that increasing rate of zirconia has a detrimental effect on strength values. The main reason is thought as the hard nature of zirconia. Because, zirconia particles as internal defects in the microstructure and they do not allow the plastic deformation of the material. After tests, fracture surfaces are observed and homogeneous distribution of the reinforcements is seen as well as good adhesion of modifiers.

Another important point is that, modulus values obtained from nano indentation, differ from the macro test results. This is considered as a consequence of pile up of material around the contact impression and viscoelasticity of the polymer.

Also, T_g of the composites is not affected from the zirconia content which signifies that zirconia do not interfere the crosslink mechanisms of the matrix.

Finally, wear test results showed that zirconia particles are efficient against to wear thanks to its hard nature. This manifest itself in less damaged after scratch surfaces. By considering all results of the material characterizations, newly designed composites can be used in automotive and aeronautic industries in the wear resistance required applications.

References

- [1] McGrath, L.M., *et al.*, 2008. Investigation of the thermal, mechanical, and fracture properties of alumina–epoxy composites. *Polymer* 49 (4), 999–1014.
- [2] Lowe, A., Hyok Kwon, O., Wing Mai, Y., 1996. Fatigue and fracture behavior of novel rubber modified epoxy resins. *Polymer* 37 (4), 565–572.
- [3] Brook, R., Cahn, R., 1991. *Concise Encyclopedia of Advanced Ceramic Materials*. Oxford, UK: Pergamon.
- [4] Richerson, D.W., 1992. *Modern Ceramics Engineering*. New York, USA: Marcel Dekker.
- [5] Bondioli, F., Cannillo, V., Fabbri, E., Messori, M., 2006. Preparation and characterization of epoxy resins filled with submicron spherical zirconia particles. *Polimery* 51, 794–798.

- [6] Medina, R., Hauptert, F., Schlarb, A.K., 2008. Improvement of tensile properties and toughness of an epoxy resin by nanozirconium-dioxide reinforcement. *J. Mater. Sci.* 43, 3245–3252.
- [7] Zaimova, D., Bayraktar, E., Katundi, D., Dishovsky, N., 2012. Design of new elastomeric composites used in manufacturing engineering. In: *Proceedings of the 14th International Materials Symposium – IMSP*, pp. 10–12.
- [8] Wetzel, B., Rosso, P., Hauptert, F., Friedrich, K., 2006. Epoxy nanocomposites – Fracture and toughening mechanisms. *Eng. Fract. Mech.* 73, 2375–2398.
- [9] Adhikari, B., De, D., Maiti, S., 2000. Reclamation and recycling of waste rubber. *Prog. Polym. Sci.* 25, 909–948.
- [10] Fiksel, J., Bakshi, B., Baral, A., Guerra, E., DeQuervain, B., 2011. Comparative life cycle assessment of beneficial applications for scrap tires. *Clean Technol. Environ. Policy* 13, 19–35.
- [11] Fang, Y., Zhan, M., Wang, Y., 2001. The status of recycling of waste rubber. *Mater. Design* 22 (2), 123–128.
- [12] Mangaraj D., 1997. *Proceedings of the International Conference on Rubbers*, p. 61. Calcutta, India.
- [13] Oliphant, K., Baker, W.E., 1993. The use of cryogenically ground rubber tires as a filler in polyolefin blends. *Polymer Eng. Sci.* 33 (3), 166–174.
- [14] Naskar, A.K., Bhowmick, A.K., De, S.K., 2001. Thermoplastic elastomeric composition based on ground rubber tire. *Polymer Eng. Sci.* 41 (6), 1087–1098.
- [15] Naskar, A.K., De, S.K., Bhowmick, A.K., 2002. Thermoplastic elastomeric composition based on maleic anhydride-grafted ground rubber tire. *J. Appl. Polymer Sci.* 84 (2), 370–378.
- [16] ASTM Spec. Tech. Publ., 1987. N184 A Glossary of Terms Relating to Rubber and Rubber Technology. American Society for Testing and Materials.
- [17] Sousa, D., Fabiula, D.B., *et al.*, 2017. Devulcanization of waste tire rubber by microwaves. *Polym. Degrad. Stab.* 138, 169–181.
- [18] Kaynak, C., Sipahi-Saglam, E., Akovali, G., 2001. A fractographic study on toughening of epoxy resin using ground tyre rubber. *Polymer* 42 (9), 4393–4399.
- [19] Menard, K.P., 2008. *Dynamic Mechanical Analysis: A Practical Introduction*. CRC Press.
- [20] Li, G., Lee-Sullivan, P., Thring, R.W., 2000. Determination of activation energy for glass transition of an epoxy adhesive using dynamic mechanical analysis. *J. Therm. Anal. Calorim.* 60 (2), 377–390.
- [21] Dorigato, A., Pegoretti, A., Bondioli, F., Messori, M., 2010. Improving epoxy adhesives with zirconia nanoparticles. *Compos. Interfaces* 17 (9), 873–892.
- [22] Irez, A.B., Bayraktar, E., Miskioglu, I., 2018. Mechanical characterization of epoxy–scrap rubber based composites reinforced with alumina fibers. In: Ralph, C., Silberstein, M., Thakre, P.R., Singh, R. (Eds.), *Mechanics of Composite and Multi-functional Materials*, vol. 6. Cham: Springer, pp. 59–70.
- [23] Ting, T.C., 1966. *The Contact Stresses Between a Rigid Indenter and a Viscoelastic Half-Space*. ASME.
- [24] Tranchida, D., *et al.*, 2007. Mechanical characterization of polymers on a nanometer scale through nanoindentation. A study on pile-up and viscoelasticity. *Macromolecules* 40 (4), 1259–1267.
- [25] Lagoudas, D.R.C., Thakre, P.R., Benzerga, A.A., 2006. Nanoindentation of cnt reinforced epoxy nanocomposites. In: Gdoutos, E.E. (Ed.), *Fracture of Nano and Engineering Materials and Structures*. Dordrecht: Springer, pp. 649–650.
- [26] Tranchida, D., *et al.*, 2006. Accurately evaluating Young's modulus of polymers through nanoindentations: A phenomenological correction factor to the Oliver and Pharr procedure. *Appl. Phys. Lett.* 89 (17), 171905.

Polymer Nanocomposite Characterization and Applications

Mahsa Shirazi, Sharif University of Technology, Tehran, Iran

Gholamreza Masoudi Rad, Petroleum University of Technology, Ahvaz, Iran

Yousef Tamsilian, Shahid Chamran University of Ahvaz, Ahvaz, Iran

© 2021 Elsevier Inc. All rights reserved.

Nomenclature

ABS	Acrylonitrile Butadiene Styrene	MWCNTs	Multi-Walled Carbon Nanotubes
AFM	Atomic Force Microscopy	Co-OMMT	Organic Montmorillonite Intercalation Cobalt Hydroxides
BF	Bright-Field	PCE	Photovoltaic Conversion Efficiency
CNT	Carbon Nanotube	PVD	Physical Vapor Deposition
CMNC	Ceramic Matrix Nanocomposite	Pt	Platinum
COD	Chemical Oxygen Demand	PBI	Poly(Benzimidazole)
CVD	Chemical Vapor Deposition	PES	Poly(Ether Sulfone)
CTE	Coefficient of Thermal Expansion	PMMA	Poly(Methyl Methacrylate)
CC	Cone Calorimeter	PAN	Polyacrylonitrile
XLPE	Cross-Linked Polyethylene	PANI	Polyaniline
DSC	Differential Scanning Calorimeter	PC	Polycarbonate
DC	Direct-Current	PI	Polydispersity Index
DO	Dissolved Oxygen	PEI	Polyetherimide
Dpa-h NPs	Dopamine-Melanin Hollow Nanoparticles	PET	Polyethylene Terephthalate
Dpa-s NPs	Dopamine-Melanin Solid Nanoparticles	PEM	Polymer Electrolyte Membrane
DSSCs	Dye-Sensitized Solar Cells	PMNC	Polymer Matrix Nanocomposite
DMA	Dynamic Mechanical Analysis	PNC	Polymer Nanocomposite
DMTA	Dynamic Mechanical Thermal Analysis	PSCs	Polymer Solar Cells
EM	Electromagnetic	PVAc	Polyvinyl Acetate
EMI	Electromagnetic Interference	PVA	Polyvinyl Alcohol
EDS/EDX/EDXS	Energy-Dispersive X-Ray Spectroscopy	SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared	SALS	Small-Angle Light Scattering
GPC	Gel Permeation Chromatography	SANS	Small-Angle Neutron Scattering
GO	Graphene Oxide	SAX/SAXS	Small-Angle X-Ray Scattering
GNP	Graphite Nanoplatelets	SPEEK	Sulfonated Poly(Ether Ether Ketone)
HVDC	High-Voltage Direct-Current	TGA	Thermogravimetric Analysis
IR	Infrared	TMA	Thermomechanical Analysis
ICPs	Intrinsically Conductive Polymers	TPU	Thermoplastic Polyurethane Adhesives
IFR/PP	Intumescent Flame Retardant/Polypropylene	TEM	Transmission Electron Microscopy
LOI	Limiting Oxygen Index	TPP	Triphenyl Phosphate
LIBs	Lithium-Ion Batteries	UV	Ultraviolet
MLC	Mass Loss Calorimeter	WAX/WAXS	Wide-Angle X-Ray Scattering
MMNC	Metal Matrix Nanocomposite	XRD	X-Ray Diffraction
MMMT	Modified Montmorillonite	XPS	X-Ray Photoelectron Spectroscopy
MMT	Montmorillonite	XRS	X-Ray Scattering

Introduction

Composite materials are a combination of two or more distinct constituents including different physical and chemical properties (Khan, *et al.*, 2016), to improve the deficient characteristics of the individual materials by combining their attractive features (Corcione and Frigione, 2012). The continuous phase with a generally greater quantity is called the matrix and the discontinuous phase embedded into the matrix is called the filler/reinforcement, both of which are separated by a distinct interface. Nano-composite materials are a subset of usual composites, in which at least one dimension of the fillers is in the range of nanomaterials (1–100 nm) (Mittal, 2015) such as nanoparticles (e.g., minerals, metallic nanoparticles, carbon nanotubes (CNTs)), sheets (e.g., exfoliated clay stacks, graphene) and fibers (e.g., electrospun nanofibers). They exhibit some unique properties attributed to the presence of small-size nanofillers with a large surface area and high aspect ratio (i.e. surface area to volume ratio), leading to an improvement in the phase interactions at the interface (Rane *et al.*, 2018). Besides, due to the presence of nanometer-scale structures in their structures, the fundamental properties such as melting point, charge capacity, and magnetic properties could be controlled without altering the chemical composition (Rane *et al.*, 2018). This is because of the size-dependency of the

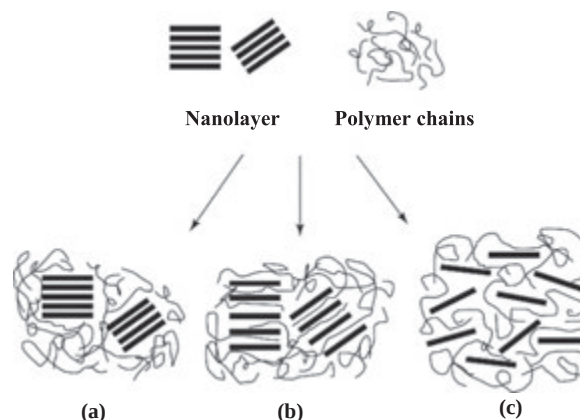


Fig. 1 Different types of nanocomposite structures: (a) unintercalated nanocomposite (microcomposite), (b) intercalated nanocomposite, and (c) exfoliated/delaminated nanocomposite. Reproduced from Alexandre, M., Dubois, P., 2000. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Materials Science and Engineering: R Reports* 28, 1–63.

nanomaterials' properties when the particle size is less than a specific value called the "critical size" (Camargo *et al.*, 2009; Din, 2019). The interface area between the nanofillers and matrix in nanocomposites is usually an order of magnitude larger than the microcomposites that makes them a suitable alternative of conventional composites, as they require a smaller amount of fillers to achieve a desired property, which makes them much lighter in weight and cheaper than microcomposites. Besides, their size-dependency properties lead to more improvement in the thermal, chemical, mechanical, optical, magnetic, and electrical properties (Khan *et al.*, 2016).

A proper choice of matrix and nanofillers plays an important role in achieving the desired properties in nanocomposite materials. Depending on the type of the matrix material, the nanocomposites could be divided into three categories of ceramic matrix nanocomposites (CMNC), metal matrix nanocomposites (MMNC), and polymer matrix nanocomposites (PMNC) (Camargo *et al.*, 2009). Polymer matrices are usually preferred to metals and ceramics, because of their low density, high-specific stiffness (Young's modulus-to-density ratio), high-specific strength (strength-to-density ratio), and ease of fabrication of complex parts on a large-scale using traditional injection molding. However, they possess poor electrical and thermal conductivities, poor mechanical properties, and a high coefficient of thermal expansion (CTE), all of which could be improved by adding an appropriate volume fraction of nanofillers (Goyal, 2017). At a low volume fraction of nanofillers (<10 wt%), a significant enhancement can be observed in thermal, mechanical, water-resistant, and barrier properties; however, in the case of high filler contents, the toughness and optical transparency will be decreased and the melt viscosity will be increased, indicating the negative effect of high fillers' volume fraction (Goyal, 2017).

The properties of the polymer nanocomposites (PNCs) depend on a vast number of factors such as the fabrication method, type/size/shape/orientation/volume fraction/aspect ratio/distribution of the nanofillers, properties of the polymer matrix, degree of mixing of two phases, nature of the interphase developed at the matrix interface, and system morphology (Jeon and Baek, 2010; Jordan *et al.*, 2005). The homogenous distribution of nanoparticles in the polymer matrix is a critical issue to achieve enhanced properties. When the nanoparticles are not well-distributed, they tend to agglomerate to each other which deteriorates the desired properties obtained by nanocomposites. Depending on the degree of nano-sized layer dispersion, three types of PNC morphologies could be obtained (Alexandre and Dubois, 2000): unintercalated/conventional/PNCs, intercalated/flocculated PNCs, and exfoliated/delaminated PNCs.

Unintercalated Polymer Nanocomposite (Microcomposite). When the polymer molecules are unable to penetrate and intercalate between the nanolayers, the phases are separated in the composite structure (Fig. 1a). The d-spacing of the layer structures is nearly identical to their pristine state and consequently, the properties of the obtained nanocomposite are in the same range as the microcomposites (Müller *et al.*, 2017).

Intercalated Polymer Nanocomposite. When the extended polymer chains can intercalate and sandwich in between the nanolayers without disturbing their ordered arrangement, a well-ordered multilayer morphology with alternating intercalated layers of polymer and clay will be formed (Fig. 1b). Consequently, the interlayer d-spacing is expanded, but only to a limited extent of 20–80 Å (Alexandre and Dubois, 2000).

Exfoliated/Delaminated Polymer Nanocomposite. When the separated individual nanolayers are uniformly dispersed in the polymer matrix, an exfoliated structure will be formed (Fig. 1c) in which the surface area between the matrix and nanofillers is larger than the case of unintercalated and intercalated polymers, and consequently, the maximum reinforcement will occur (Bhattacharya *et al.*, 2007). The d-spacing between the layers is significantly expanded up to 10 nm or more, above which the interaction forces between the layer structures diminish. Achieving an exfoliated structure of the PNCs is the ultimate goal of most researchers because of obtaining the maximum improvement in the nanocomposite properties. The exfoliated nanocomposites could be subdivided into three categories of ordered, disordered, and partial exfoliated PNCs, depending on the relative change in layer spacing and orientation (Alexandre and Dubois, 2000). When the ordered and parallel arrangement of the nanolayers is preserved

during the dispersion in the polymer matrix, a homogeneous morphology with individual separated layers is formed which is called the ordered exfoliated nanocomposite, while in the case of disordered exfoliation, the ordered arrangement of the nanolayers is completely disrupted to form a homogeneous and random dispersion of individual nanolayers in the polymer matrix. The partially exfoliated nanocomposites behave as an intermediate of the intercalated and exfoliated structure since it is associated with dispersed exfoliated layers and small stacks of intercalated layers, making its morphology as a middle of the case of exfoliation and intercalation (Liu *et al.*, 2006). It should be mentioned that exfoliation requires high shear and high temperature which is a great challenge for the materials.

Depending on the type of PNC morphology, different physical and mechanical properties will be obtained (Liu *et al.*, 2006). To reach an intercalated or exfoliated structure, it is required sometimes to modify the surface of the nanofillers with the chemical groups that are compatible with the polymer, to minimize or even avoid the agglomeration of nanoparticles which has a detrimental influence on the nanocomposite structure and properties (Goyal, 2017).

PNCs have a wide range of applications in various fields such as food packaging, aerospace industries, automobile sectors, oil and gas pipelines, and bone repairs, etc. The purpose of this article is to first describe different types of nanocomposites with a focus on the PNCs followed by a detailed explanation of their characterization techniques (structural analysis, thermal properties, mechanical properties, and electrical properties) and their industrial applications (biomedical and tissue engineering applications, energy-related applications, corrosion protection applications, ballistic, aerospace, and automobile applications, ultraviolet (UV) protection applications, sensors applications, smart PNCs applications, adhesive applications, and flame retardant PNCs).

Different Types of Polymer Nanocomposites

As it was mentioned before, the nanocomposite materials can be classified into three categories of CMNCs, MMNCs, and PMNCs, each of them is explained below (Khan *et al.*, 2016).

Ceramic Matrix Nanocomposites (CMNC)

Ceramic is a brittle material that can be easily fractured under a crack propagation. The incorporation of a ductile phase in the ceramic matrix to form a ceramic nanocomposite improves its mechanical properties such as hardness and fracture toughness, attributed to the interactions between the matrix and reinforcements. To deeply understand the structure-property relationship in the CMNC, the ratio of surface area to the volume of the reinforcement materials is a key factor. Some of the common methods of fabricating the CMNCs are conventional powder method, polymer precursor route, spray pyrolysis, vapor techniques (Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD)), and chemical methods such as the sol-gel process, colloidal and precipitation approaches, and template synthesis (Camargo *et al.*, 2009; Liu *et al.*, 2004; Thompson *et al.*, 2003). Some of the common CMNCs are $\text{Al}_2\text{O}_3/\text{SiC}$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{TiO}_2/\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{CNT}$, $\text{TiO}_2/\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4/\text{CNT}$, SiO_2/Ni , SiO_2/CNT , ZnO/Co , $\text{MgAl}_2\text{O}_4/\text{CNT}$, and MgO/CNT (Parameswaranpillai *et al.*, 2016).

Metal Matrix Nanocomposites (MMNC)

The reinforcement of nanoparticles in the ductile metal/alloy matrix forms MMNCs with entirely different physical, chemical, and mechanical properties compared to the individual metals and nanoparticles. A significant improvement in the mechanical properties of the metal nanocomposites is because of the interactions between the nanoparticles and dislocations when the nanoparticles act as a barrier in dislocation movements. From the common fabrication methods of MMNCs, it can be referred to the spray pyrolysis, liquid metal infiltration, vapor techniques (CVD and PVD), rapid solidification, electrodeposition, and chemical techniques such as colloidal and sol-gel methods (Camargo *et al.*, 2009). Some examples of the common MMNCs are $\text{Fe}/\text{Al}_2\text{O}_3$, $\text{Ni}/\text{Al}_2\text{O}_3$, Fe/MgO , Al/CNT , and Mg/CNT .

Polymer Matrix Nanocomposites (PMNC)

PMNCs involve the addition of one-dimensional (such as nanotubes and fibers), two-dimensional (such as layered materials), and three-dimensional (such as spherical particles) nanofillers in the polymer matrix. The addition of a low volume fraction of nanofillers in the polymer matrix leads to outstanding properties such as barrier resistance, flame retardancy, wear resistance, easy production, high elastic stiffness and strength, lightweight, ductile nature, and generally excellent magnetic, electrical, mechanical, and optical properties, although, they possess lower modulus and strength compared to the case of ceramic and metal nanocomposites. Some of the common fabrication methods of PMNCs are in-situ polymerization, in-situ intercalative polymerization, intercalation of polymer/pre-polymer from solution, direct mixing of polymer and fillers (particulates), mixing filler materials during electrospinning, melt intercalation, melt mixing, template synthesis, and sol-gel process. Some examples of the common PMNCs are thermoplastic polymer/layered silicates, thermoset polymer/layered silicates, polyester/ TiO_2 , polymer/ CNT , and polymer/layered double hydroxides.

The major component in a PMNC is the polymer itself. A vast variety of polymers is used in the preparation of PMNCs, three common types of them are thermoplastics, thermosets, and elastomers. The main difference between the thermoplastic and thermoset polymers is their different behavior against heating attributed to the difference in their molecular structure. Thermoplastic polymers soften to a mobile and flowable state under heating and can be shaped into a useful object and harden/solidify under cooling, while holding their shape (Peters, 2014). Hence, they could be remolded and recycled without affecting the properties. The curing process is completely reversible since no cross-linking takes place. In contrast, the thermoset polymers do not soft or melt under heating and retain their strength and shape, but breakdown chemically at high temperatures. They exhibit elasticity and chemical resistance and withstand elevated temperatures from ambient to above 450 °F, without loss of structural integrity. The curing process is irreversible, attributed to the cross-linking of polymers together. Thermoset polymers are generally rigid and brittle compared to thermoplastics, possessing improved mechanical properties, high chemical and heat resistance properties. The third type of polymers is elastomers that are elastic or rubberlike with high elongation and flexibility against breaking and can be classified into thermoset elastomers and thermoplastic elastomers that the first type is not melted when heated while the second one is melted. The thermoset-based nanocomposites are generally the most common type used in many applications; however, the thermoplastic-based nanocomposites have recently gained the attraction of many researchers in both industry and academia (Koo, 2006), including the automotive and packaging area (Lampman, 2003).

The reinforcing materials in the PNC structures can be classified based on their dimension into three categories of one, two, and three-dimensional materials. The three-dimensional nanofillers, also called isodimensional nanoparticles, contain three dimensions in the nano-scales, some examples are spherical silica, metal particles, and semiconductor nanoclusters (Herron and Thorn, 1998). In the two-dimensional nanofillers, two dimensions are on the nanometer scale and the other on a larger scale, some examples are CNTs and cellulose whiskers. Carbon nanofibers, ranging from disordered “bamboo-like” to highly ordered “cup stacked” graphite structures with a diameter ranging from 50 to 200 nm, are a kind of two-dimensional nanofillers employing in a variety of polymer matrix compounds, including both thermoset polymers (such as epoxy, polyimide, and phenolic) and thermoplastic polymers (such as polypropylene, polystyrene, poly(methyl methacrylate)) PMMA, Nylon 12, and PEEK (Sandler *et al.*, 2003). The one-dimensional nanofillers with the one dimension in the nanometer range and the others in the larger scale, and the nanocomposite containing these nanofillers are called polymer-layered nanocomposite. Polymer layered silica nanocomposites are a type of one-dimensional nanocomposites with a significant improvement in their properties such as possessing high moduli, high strength and heat resistance, low flammability, low gas permeability, and high biodegradability. The ability of the layered silicate to disperse into the individual layers along with the ability of fine-tuning their surface chemistry lead to the formation of strong interactions between the nanolayers and the polymer matrix, forming an intercalated or exfoliated nanocomposite.

A brief description of the different types of nanocomposites, their properties, synthesized methods, and common examples are given in Table 1.

Characterization and Analysis of Polymer Nanocomposites

After preparation of the PNCs by a proper method, the obtained material should be characterized to determine the degree of nanoparticles' dispersion in the polymer matrix and to analyze the thermal, mechanical, and electrical properties to find out whether it is desired for our purpose or not. Therefore, the nanocomposite characterization is divided into structure analysis, using a variety of microscopic and spectroscopic techniques, and property measurement (i.e., thermal, mechanical, electrical), depending on the individual applications (Koo, 2006). The main challenge in characterizing the nanostructures is the dependency of their physical properties on the size and shape. The surface modification of the small size (i.e., diameter and length) nanostructures is rather difficult and also it is not possible to apply the common well-established techniques for their characterization. Consequently, some specialized techniques are required for identifying and analyzing individual nanostructures and quantifying their properties. In what follows, the methods of PNC characterization are described based on three categories of structural/morphological characterization, thermal characterization, and mechanical characterization.

Structural and Morphological Characterization

The methods of characterizing the structure of PNCs can be generally divided into four categories of microscopic techniques, spectroscopic techniques, scattering techniques, and chromatography, each of which has several subdivisions which are described in detail below.

Microscopic techniques

The microscopic techniques usually provide a suitable picture of nanocomposite morphology that like a microscope, could give an image of the structure.

Optical microscopy

Optical microscopy is usually a useful tool for characterizing the microcomposite structures in the cases of very thin samples with a transparent matrix. So, it is not a suitable tool for characterization of the nanosize materials.

Table 1 Properties, synthesized methods, and common examples of ceramic, metal, and polymer nanocomposites

<i>Types with Features</i>	<i>Nanocomposites</i>	<i>Synthesis method</i>
1. Ceramic Advantages: Good wear resistance High thermal and chemical stability Disadvantages: Brittle Low toughness	Enhanced mechanical properties including fracture toughness, stiffness, and strength	Conventional powder method Polymer precursor route Spray pyrolysis Vapor techniques (CVD and PVD) Chemical methods (sol-gel process, colloidal and precipitation approaches, template synthesis)
2. Metal Advantages: Electrical and heat conductive Ductile toughness with high strength and modulus Disadvantages: Highly corrosive	Wear and chemical resistance High electrical and thermal stability High strength in shear/compression processes	Spray pyrolysis Liquid metal infiltration Rapid solidification Vapor techniques (CVD and PVD) Electrodeposition, Chemical methods (colloidal and sol-gel processes)
3. Polymer Advantages: Easy production process Lightweight Ductile Disadvantages: Low strength and modulus	Mechanical strength Enhanced magnetic, electronic, optical, and catalytic properties Flame retardancy Low gas permeability high biodegradability	In-situ intercalative polymerization Intercalation of polymer/pre-polymer from solution Direct mixing of polymer and fillers Melt intercalation Template synthesis Sol-gel process

Electron microscopy

In this method, the images are obtained by using high-energy electrons with a wavelength ($0.025\text{--}0.1\text{ \AA}$) much smaller than that of the light, allowing for imaging the small objects in the nanometer scale. The electron interactions with the samples give detailed information on their structure. This method is based on the wave-particle duality of electrons and it is widely used when a much larger magnification than that of light microscopic techniques is required, as the particle size is smaller than the wavelength of the visual light (Bhattacharya *et al.*, 2007). The three main electron microscopic techniques for characterizing the nanocomposite morphology are scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

Scanning electron microscopy (SEM)

In this method, a focused electron beam is produced by an electron gun to scans over a specimen with an electrically conductive surface. In the case of electrical isolator surfaces like most of the polymeric materials, the surface of the sample should be coated with a layer of a conductive material such as gold or carbon, or the environment of the sample should be conductive. As a result of the interaction between the electron beams and the atoms of the specimen surface, various signals will be produced and detected by a detector and the scanned image of the surface will be obtained by reproducing the varying intensity of the detected signals on a screen. SEM method is one of the most frequently used techniques of nanostructured surface characterizations with a high resolution of $1\text{--}5\text{ nm}$ and a large depth of field which makes the images appear three-dimensional (Oksman and Moon, 2014). The main limitation of this method is the surface scanning of the specimen without characterizing the inner parts which can be partially addressed by using cold temperature fracture or ultra-microtoming.

Transmission electron microscopy (TEM)

In this method, the high energy electrons are emitted from an electron gun and transmitted through an ultrathin section of the specimen. Two or more condenser lenses are inserted below the gun to demagnify the emitted beam and control its diameter when hitting the specimen that is held inside an objective lens just below the condenser lenses. The objective lens in TEM is critical as it determines the limit of image resolution. As the electron beam hits the specimen, an image will be formed as a result of electron scattering. In bright-field (BF) imaging mode, for instance, the image is formed by the unscattered electrons; the thicker or higher density regions of the specimen strongly scatter electrons and will appear darker in the image since the highly scattered electrons are stopped by the objective aperture (Oksman and Moon, 2014). The TEM method provides direct visual information of the morphology, molecular arrangement, and spatial distribution of the phases along with detecting structural defects within the selected area of the sample. The better resolution of the TEM method (0.2 nm) compared to the SEM (2 nm) as a result of higher electron energy, along with providing the internal information of the specimen by TEM compared to the surface information by SEM, make the TEM method more applicable than SEM (Koo, 2006). In the case of PNCs, TEM is the most suitable microscopy

method to provide direct imaging of the extremely small size nanoparticles along with determining the nanofillers distribution and dispersion (including uniformity and non-uniformity) as it analyzes the through-thickness of the material. By applying today's TEM devices, the chemistry of a single nanocrystal can be directly identified because of providing the atomic resolution lattice images and chemical information at a spatial resolution of 1 nm. Some of the main limitations of the TEM method are the high cost of analytical instruments, the difficult process of sample preparation, the inability of scanning heterogeneous samples, and the inability of detecting the intercalated and exfoliated nanocomposites, attributed to the inability of measuring the d-spacing between the nanolayers (Reifarth *et al.*, 2018). The sample preparation is critical to obtain a good resolution TEM image. Some of the basic requirements are that the sample should be thin enough to be transparent to the electron beam and also it should be clean without any damage or contamination. The common methods of sample preparation are ion milling (for all kinds of materials), electropolishing (for conductive materials), and crushing powder (for all materials but neglecting the detail of microstructural). The sample is usually prepared by ultra-microtoming at room temperature, when the polymer T_g is higher than the room temperature and at low temperature, when the polymer T_g is lower than the room temperature (Morgan and Gilman, 2003).

Atomic force microscopy (AFM)

In this method, by scanning the AFM probe with a typical curvature radius of 10 nm via operating modes of contact or intermittent-contact over the composite surface, the interactive force between the atoms of the probe and those of the specimen is measured and the interaction response is monitored, resulting in a topography image. The forces applied to the specimen are typically in the order of 10^{-9} N, which is small enough, ensuring no damage to the specimen (Bhattacharya *et al.*, 2007). By maintaining the feedback on the amplitude of the probe variation in the intermittent-contact mode, the nanoparticle distribution within the PNC can be obtained using phase imaging that records the phase lag (i.e., delay) of the cantilever oscillation, relative to the signal sent to the cantilever's piezo driver. The phase lag is sensitive to variations in material properties such as adhesion, viscoelasticity, etc., and a contrast will be created between the different material components within nanocomposites. In the phase images, the harder phase appears lighter due to the higher phase offset, whereas the softer phase appears darker. The edges can be also highlighted via phase imaging, providing a clearer observation of fine features such as grain edges. The AFM method is a relatively new technique in characterizing the nanometer-scale features of the surface chemistry, especially in the case of nanocomposites with an atomic resolution of 0.2–0.5 nm (Braga and Ricci, 2004; Bandyopadhyay *et al.*, 2008). Considering the nature of the AFM method as a surface characterizing technique, it is necessary to image multiple sections through the thickness of the nanocomposite to characterize the nanoparticle distribution through the thickness (Marinello *et al.*, 2019; Kumar *et al.*, 2014). Despite the SEM and TEM methods which are only applicable for conductive samples, the AFM can image both conductive and nonconductive materials usually under atmospheric conditions (Oksman and Moon, 2014).

Spectroscopic techniques

To analyze the chemical structure of macromolecular materials such as functional groups, structural conformation, and component concentrations, spectroscopic techniques are used. These methods involve the interaction of the sample molecules with electromagnetic (EM) radiation and an image will be obtained by monitoring the changes in energy states of molecules in response to EM radiation as the atom/molecule's energy will exceed from an initial state to a higher level by adsorbing energy.

Fourier transform infrared (FTIR) spectroscopy

In this method, a beam of infrared (IR) radiation emitted from a glowing black-body source is passed through the specimen. By exposing the specimen's molecules to the IR radiation, they absorb some specific frequencies of the energy as the unique characteristic of the sample, and the unabsorbed frequencies will be transmitted and recorded by a detector, enabling the identification of the absorbed ones (Berthomieu and Hienerwadel, 2009; Marley *et al.*, 2001). The energy of the specimen's molecules will be risen to a higher level by adsorbing the IR energies, resulting in their vibration at greater amplitudes, depending on the atomic weight and the force constant of the atom bound to its environment. These vibrational frequencies correspond to the region within the IR spectrum and the unknown molecules will be then identified by matching the absorption wavelength/frequency to those already known (Li *et al.*, 2006; Suhail *et al.*, 2019).

Nuclear magnetic resonance (NMR)

In this method, the specimen is exposed to a magnetic field, hitting by radio waves. The atoms' nucleus of a sample is in spinning or resonance motion, inducing a magnetic moment that is aligned randomly, in the absence of a magnetic field and regularly, in the presence of it. By exposing the positively charged nucleus to the radio waves of the magnetic field, the magnetic field of the nucleus will resonate (Papon *et al.*, 2012). The response of the atomic nucleus to the magnetic field, which is due to the shielding of a particular nucleus by the neighboring nuclei, is measured in the form of a spectrum (Munoz and Greenbaum, 2018; Drzeżdżon *et al.*, 2019).

Ultraviolet spectroscopy

In this method, light is passed through a sample at a specific wavelength (200–400 nm) in the UV or visible spectrum. The molecules containing bonding and non-bonding electrons can absorb energy in the form of UV/visible light to excite these electrons between the energy levels, corresponding to the molecular orbitals. In particular, the transitions involving p orbitals and

lone pairs (n = non-bonding) are more important (Zhang *et al.*, 2013; Munk and Aminabhavi, 1989). The UV-visible spectroscopy is mostly used for identifying the conjugated systems that tend to have a stronger absorption. The shape and absorbance of the spectra can be measured with good precision. The measurement of absorbance provides useful information for calculating the concentration of macromolecules; however, it is not useful in obtaining structural information (Li *et al.*, 2006).

Energy-dispersive X-ray spectroscopy (EDS/EDX/EDXS)

When a sample is exposed to the SEM electron beam, electrons are ejected from the atoms of the sample surface. The resulting electron holes are filled by electrons from a higher state, and an x-ray is emitted to balance the energy difference between the two electrons' state. In the EDS technique, these emitted x-rays are detected and their relative abundance is measured versus the energy, to determine the elemental composition of the sample. The spectrum of EDS microanalysis contains both semi-qualitative and semi-quantitative information. The emitted X-rays and their intensity distribution are a characterization of the element type and atom densities, respectively (Son *et al.*, 2020). Generally, the EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample since each element has a unique atomic structure allowing a unique set of peaks on its EM emission spectrum (Hosseini *et al.*, 2015; Schmidt *et al.*, 2019).

Scattering techniques

The scattering methods are used to analyze the morphology and structural evolutions of micro/nanocomposite materials. The three main scattering techniques used in PNCs are X-ray scattering (XRS) (wavelength between 0.01 and 0.2 nm), light scattering (wavelength between 350 and 700 nm), and neutron scattering (wavelength between 0.1 and 1 nm), depending on the electron densities, optical densities/refractive indices, and nature of the scattering nucleus, respectively. The main difference between these methods is the length scale probed, relating to the wavelengths of the scattering beam. The similar and small wavelength of X-ray and neutron scattering indicates their applicability for the same structure size, while large structures could be investigated via light scattering because of their larger wavelength (Chen *et al.*, 2018).

X-ray scattering

The XRS techniques can differentiate between the crystalline and semi-crystalline materials and consequently, making them useful in analyzing the solid materials. Depending on the magnitude of the angle deviation from the direct beam, the XRS can be divided into two subcategories of small-angle (SAX) and wide-angle (WAX) regions. The exact difference between the region areas of SAX and WAX is still ambiguous. Alexander in 1969 considered any scattered beam larger than 2° or 3° as a WAX region, while other researchers such as Morgan and Gilman in 2003 classified the angles greater than 1° as a WAX region (García-Gutiérrez *et al.*, 2007).

Wide-angle X-ray scattering (WAX/WAXS)

The WAX method is a method of investigating the partially ordered materials. The crystalline structure of the PNCs along with the degree of nanofillers dispersion in the polymer matrices could be characterized via this method by measuring the d-spacing between the ordered crystalline layers of the nanolayers (Chen *et al.*, 2018). The d-spacing is measured based on Bragg's law with the following equation:

$$\sin\theta = \frac{n\lambda}{2d} \quad (1)$$

Where d is the spacing between the interlayers, λ is the x-ray wavelength, n is a positive integer, and θ is the angle of incidence. The intensity of the diffracted x-ray is measured as a function of the diffraction angle 2θ and the specimen's orientation. The specimen's crystalline phases and its structural properties could be measured using the diffraction pattern (Bhattacharya *et al.*, 2007). An initial assessment of the structure and morphology of the PNCs can be made by observing any changes in the d-spacing. One of the main advantages of the WAX method compared to the electron microscopy methods is that it does not require any sample preparation and consequently, it is a non-destructive method, indicating the wide usage of this technique in materials characterization (Bishnoi *et al.*, 2017).

Small-angle X-ray scattering (SAX/SAXS)

In this method, the sample is irradiated by a well-defined, monochromatic x-ray beam with the purpose of structural characterization of solid and fluid materials in the nanometer range (0.5–50 nm). The very low scattering angles of the SAX method, make it possible to obtain the structural information of the nonhomogeneous specimens from the intensity distribution of the scattered beam (Demchenko and Riabov, 2017). Both monodisperse and polydisperse systems can be analyzed via the SAX method. In the monodisperse systems, the size, shape, and internal structure of the particles can be determined, while in the polydisperse systems, a size distribution can be only obtained when the shape and internal structure of the particles are the same (Cser and Bhattacharya, 2003; Sakurai, 2017). SAX method can be used in structural characterization of different materials such as suspended nanopowders, polymer films and fibers, catalyst surface per volume, microemulsions, and liquid crystals (Baeza *et al.*, 2016).

X-ray diffraction (XRD)

The diffraction process is only possible in cases where the wavelength of the wave motion is in the same order of magnitude of the repeat distance between the scattering centers. XRD is a convenient and rapid method for initial characterization of

nanocomposites structure and morphology, by monitoring the intensity, position, and shape of the basal reflections from the distributed nanofillers (Demchenko *et al.*, 2017). The distance between the interlayers could be determined from this method as an indication of the success or failure of the ion-exchange process during the nanofiller modification or the intercalation/penetration of the polymer chains. It is also possible to identify the non-intercalated, intercalated, and exfoliated structures via the XRD method, when there is no change in peak, an increase in peak, and no peak, respectively (Abhilash *et al.*, 2016).

Light scattering

This technique involves the light scattering through dilute solutions, as a widely used technique in polymer science to determine the molecular weight, second virial coefficient as an intermolecular interaction parameter, and the radius of gyration of high molecular-weight polymers (Yadav *et al.*, 2017).

Small-angle light scattering (SALS)

By using the SALS method, it is possible to determine the relationship between the structure and properties of the PNC in both solid and melt phases. The structural evolution of the nanocomposites could be investigated by determining the shape and size of the crystalline nanostructures (Shibayama *et al.*, 2005; Oberdisse *et al.*, 2017; Jouault and Jestin, 2016).

Neutron scattering

Small-angle neutron scattering (SANS)

The underlying principles of the SANS method are similar to the SAXS and SALS techniques, except that of the wavelength, and consequently, the length scale is the probing parameter. In this method, a neutron approaches an atomic nucleus the nuclear forces repel it, resulting in a scattered neutron beam. The structural evaluation of the nanocomposite samples will be then possible as the scattered neutron interferes with other waves.

Chromatography

Gel permeation chromatography (GPC)

The GPC method is conducted on polymer solutions, resulting in the hydrodynamic volume of the dissolved polymer. In this method, the polymer is first dissolved in a suitable solvent and the obtained solution is injected into a porous gelled column with a gelled material such as cross-linked polystyrene, dextran, polyacrylamide, or even styrene-divinylbenzene copolymer (Styragel) (Bhattacharya *et al.*, 2007; Bhattacharya, 2016). To determine the polymer molecular weight, the porosity of the column should be varied. Different types of average molecular weights can be determined by the GPC technique including the weight average molecular weight (M_w) (based on the concept of the highest "concentration" of molecular weights), number average molecular weight (M_n) (the ratio of total molecular weights of all samples and total number of polymer molecules, and the viscosity average molecular weights) (M_v) (based on the viscosity) (Yei *et al.*, 2004). Besides the determination of molecular weight, it is also possible to specify the polydispersity index (PI), and the branching index. The PI, calculated from the ratio of M_w and M_n , is an indication of the molecular weight distribution in the polymer. A PI of 1 corresponds to a monodisperse material, whereas higher values correspond to a wider distribution of the molecular weights of the macromolecules. The usage of suitable filters before the test is necessary for the GPC analysis of filled materials, such as PNCs, where the clay will not dissolve in the organic solvent (Zhen and Zheng, 2016).

Thermal Properties

Characterization of the thermal properties involves the techniques in which a property of a specimen is continuously measured through a pre-determined temperature profile to analyze the changes in the heat content (enthalpy) or the sample's specific heat (Kumar *et al.*, 2019).

Differential scanning calorimeter (DSC)

In this method, as one of the most common thermal analysis techniques for nanocomposite materials, different parameters could be measured during the thermal heating such as glass transition temperature (T_g), melting, crystallization, and curing (Lionetto and Maffezzoli, 2008). Considering T_g as the Brownian motion of the polymer chains during the transition from the glassy to the rubbery state and the relaxation of dipoles associated with it, the presence of nanofillers in the PNC structures leads to the enhancement of T_g that can be measured via the DSC technique. The T_g enhancement is attributed to the encapsulation of the intercalated polymers in the nanofillers galleries, preventing the partial movement of the polymer chains (Chattopadhyay and Webster, 2009; Kazakova *et al.*, 2018). By applying thermal energy, the enhancement of enthalpy and specific heat of the sample can be also measured by the DSC technique; regarding the point that the changes in specific heat are slow at a specific state, while changes sharply during a state alteration, inducing some physical or chemical changes in the sample (such as melting or decomposition) accompanied by a change in enthalpy in the form of the latent heat of fusion, the heat of reaction, or others (Rahman *et al.*, 2017).

Thermogravimetric analysis (TGA)

In this method, the sample is continuously weighted in a controlled atmosphere (e.g., air or nitrogen) as the temperature is linearly increased. The filler content of a PNC material along with its thermal stability improvement during temperature changes can be quantitatively measured via the TGA method. The improvement of thermal stability, which means that the thermal degradation occurs at a higher temperature, is attributed to the formation of a char that hinders the out-diffusion of the volatile decomposition products due to the permeability reduction and is usually observed in exfoliated or intercalated nanocomposites (Leszczyńska *et al.*, 2007). The improvement in thermal stability of the nanocomposites is somewhat dependent on the amount of filler content; at low filler content of about 1 wt%, the amount of exfoliated nanofillers is not enough to enhance the thermal stability through char formation (Alexandre and Dubois, 2000); at intermediate filler content of about 2–4 wt%, more exfoliated nanofiller is formed and the thermal stability is improved attributed to the easy and effective formation of char; and finally, at high filler content of up to 10 wt%, the intercalated structure is the dominant population and the high thermal stability is not maintained due to the different morphology of the nanocomposite even at high quantity formation of char (Taha, 2017). Generally, the most important factors with a critical role in the thermal degradation of PNCs are the chemical nature of the polymers, the type of nanofillers, and their modification route (Kausar, 2018; Loganathan *et al.*, 2017).

Cone calorimeter (CC)

In this method, the small sample of material is burned in the device to evaluate the sample reaction to the fire via direct or indirect measuring of various parameters such as time to ignition, ignitability, rate of surface flame spread, heat release rate per unit area, cumulative heat release, mass loss rate, total mass loss, effective heat of combustion, combustion products, smoke evolution, smoke obscuration, and evolution of toxic gases (Shen *et al.*, 2017; Hanna *et al.*, 2018; Zanetti *et al.*, 2002).

Mass loss calorimeter (MLC)

The MLC method only determines the mass loss rate and ignitability at a specific heat flux condition and is a suitable replacement for the cone heater cell assembly in the CC. As a stand-alone instrument, the MLC could be considered as a quality control tool, containing two parts of the cone heater assembly and the control assembly. The combustion products and their toxicity can be also measured via this system. The approximate value of the heat release rate can be estimated from the mass loss rate data if the effective heat of combustion (ratio of heat release rate and mass loss rate) is known (Koo, 2006).

Mechanical Properties

The mechanical properties of PNCs are strongly dependent on the type and properties of matrix and fillers, filler distribution in the matrix, interfacial bonding and interaction between filler and matrix, the aspect ratio of filler, and the fabrication method (Krishnaiah *et al.*, 2017). As noted earlier, the surface modification of the nanofillers could strongly promote the filler distribution and their interfacial adhesion to the matrix material. The methods of mechanical analysis measure the tensile strength, tensile modulus, and elongation, which are a measure of the material's strength under the tensile loading, material's resistance to the deformation, and material's stretching/deformation before the break, respectively (Shah *et al.*, 2016). A failure in the composite structure usually initiates with a crack formation and by adding nanofillers with a smaller size than the crack length, the toughness and strength of the sample will be improved, as the nanoparticles fill the cracks (Sun *et al.*, 2018). Besides, the aspect ratio could be increased via the addition of a high volume ratio of nanofillers to the polymer matrix, leading to an increment in Young's modulus and yield strength, although above an optimum concentration the nanofillers aggregation induce a negative effect on the mechanical properties of the nanocomposites (Bhattacharya, 2016).

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical properties of PNCs depend on the nanoparticle orientation, polymer morphology, and strength of interphase interactions of the nanofillers, all of which can be improved by the introduction of macromolecular compatibilizers (Candan *et al.*, 2016). By the DMTA technique, it is possible to measure the storage modulus (E') and loss modulus (E'') as the two material's ability in returning/storing the mechanical energy, and in dissipating energy, respectively, as a function of temperature (Jayanarayanan *et al.*, 2017). Some useful information about the nanofillers' orientation, exfoliation, and interphase interactions could be also measured indirectly (Lionetto and Maffezzoli, 2009).

Thermomechanical analysis (TMA)

The TMA method is used to measure the expansion/contraction of cross-linked or filler materials and the coefficient of thermal expansion of nanocomposite materials (Fu *et al.*, 2008; Krump *et al.*, 2006). The lower value of CTE is an indication of better thermal properties of nanocomposites and the degree of CTE reduction depends on the nanoparticle rigidity, particle dispersion/distribution, stress transfer to nanolayers, and retardation of chain segmental movement through the incorporation of modified nanolayers (Burgaz, 2016).

Dynamic mechanical analysis (DMA)

In this method, an oscillating force is applied to the sample at a specific temperature, resulting in a deformation that is measured to determine the sample stiffness, sample storage modulus, and viscoelasticity. Furthermore, the damping properties of the material can be determined by measuring the time lag in the displacement compared to the applied force (Liu *et al.*, 2003; Chauhan *et al.*, 2018).

Electrical Properties

The electrical properties of common polymers are usually low than 10^{-14} S/m, indicating their inability in conducting electricity. These properties could be enhanced by introducing conductive nanoparticles/nanotube/fibers into the polymer matrices in the form of nanocomposite structure (Mutiso and Winey, 2015). The degree of electrical conductivity of the obtained nanocomposite is strongly dependent on the volume fraction of conductive fillers. In the case of low-filler loadings, the conductivity of the nanocomposite is nearly close to that of the polymer matrix. Increasing the filler loading leads to a slight increment in the electrical conductivity until reaching a critical volume fraction, at/above which a sharp increase is observed. Just above a percolation threshold, the nanofillers begin to form some three-dimensional conductive networks which assist in electrons flow from one end to another end of the sample (Allaoui *et al.*, 2002). Depending on the shape, size, and aspect ratio of the nanofillers, the onset of percolation and the required nanofillers concentration may be different (Hashemi and Weng, 2016). As an instance, the required particle concentration for the percolation threshold for fiber is several orders of magnitude less than the case of spherical particles, indicating the inverse relation between the percolation threshold and the aspect ratio of nanotube/nanofibers (Bandaru, 2007). Above the percolation, a sharp increase of several orders of magnitude is observed in the electrical conductivity. A decrease in the aspect ratio of the nanofillers in a given nanocomposite due to their poor dispersion or agglomeration results in a significant difference between the percolation threshold and the highest obtained electrical conductivity (Otaegi *et al.*, 2019). Generally, the percolation threshold is dependent on the chemical, physical, and geometrical parameters such as the type of polymer matrix (amorphous or semicrystalline) and nanofillers, surface treatment of nanofillers, fabrication method, spatial distribution/dispersion, and aspect ratio (Tschöpe and Birringer, 2001). Despite the positive effect of chemical functionalization of the nanofillers on their better dispersibility and improvement of their mechanical properties by forming stronger bonds between the matrix and the nanotube, it usually reduces the electrical conductivity of the nanocomposites, attributed to their tendency of scattering electrons instead of transporting. Moreover, the chemical functionalization tends to reduce the aspect ratio of the nanotubes and consequently, the percolation threshold will be increased (Haghgoo *et al.*, 2019).

Industrial Applications of Polymer Nanocomposites

Recently, PNCs have found huge commercial potential in many areas, as they have superior properties in comparison with traditional polymers. The tremendous properties of the PNCs and their flexible functionalities make them attractive for different industrial fields of application from energy storage to biomedicine, some of the common ones are illustrated in Fig. 2 (Mansor and Akop, 2020; Klefenz, 2004; Sunday *et al.*, 2012; Hossain and Hoque, 2018; Lau *et al.*, 2018; Vatanpour and Safarpour, 2018; Joshi and Kumar, 2018; Bharathidasan *et al.*, 2020; Zare and Shabani, 2016; Anagri *et al.*, 2019; Ansari *et al.*, 2015).

Biomedical and Tissue Engineering Applications

The desirable properties of biopolymer-based materials are attractive for biotechnology applications such as fighting and preventing diseases, using atomic/nano-scale of the functional materials. In this view, biopolymer-based nanocomposites are of great scientific importance in tissue engineering to repair/remove injured tissue/organ. Numerous researches have been done on the applicability of PNCs in medical fields including nerve tissue repairment (Balint *et al.*, 2014), bone regeneration nanocomposite scaffold (Hajiali *et al.*, 2010; Pina *et al.*, 2015), and artificial skin (Suzuki *et al.*, 2000). In tissue engineering, scaffolds are based on a temporary artificial matrix that provides a three-dimensional support structure for cell seeding, proliferation, and new tissue formation (Kumar *et al.*, 2018).

The other important application of PNCs in biotechnology is the smart packaging of food (Pavlović and Pavlović, 2021). This type of packaging offers significant environmental and economic advantages as they are biocompatible/biodegradable and a great gas barrier (Zafar *et al.*, 2016; Cui *et al.*, 2015). The biodegradable nature helps to recover the lacking assets (i.e., degradability) of conventional petroleum-based plastic packaging materials (Duncan, 2011). The incorporation of metal with a strong anti-microbial activity like Zinc (Lemire *et al.*, 2013), clay, or graphene as nanofillers produces a nanocomposite for food packaging application with a maze structure that greatly reduces the permeation of gases (Burdock, 2007; Müller *et al.*, 2017). On the other hand, the use of platelet-shaped nanofillers in a polymer matrix such as layered silicate nanoclays (e.g., montmorillonite (MMT) and kaolinite) produces a tortuous path as a gas barrier structure for liquids and gases and results in a delay in the oxidation of food and beverages. The barrier performance of PNC packages is illustrated in Fig. 3.

Another application of PNCs is the detection and treatment of cancer in terms of identifying tumor cells and selective irradiation of targeted tumor areas (Liu *et al.*, 2014; Peng *et al.*, 2015; Liao *et al.*, 2017; Feldman, 2019).



Fig. 2 Common industrial applications of polymer nanocomposites.

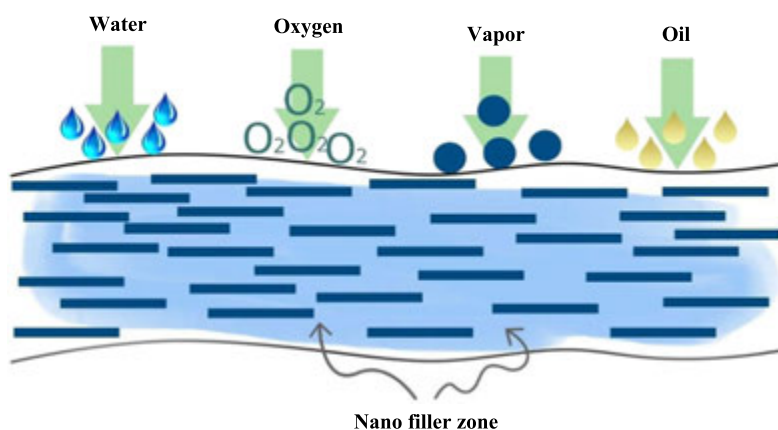


Fig. 3 Barrier performance of polymer nanocomposite packages. Reproduced from Duncan, T.V., 2011. Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal of Colloid and Interface Science* 363, 1–24.

PNCs also have the potential of being a carrier for the controlled release of drug delivery. Liu *et al.* demonstrated the drug delivery of polymer-clay nanocomposites which were prepared by reactive melt extrusion. They proved that the addition of nanoclays into the polymer matrix enhances the drug delivery efficiency of the PNC (Liu *et al.*, 2020).

Energy-Related Applications

In recent years, the increase in the global population has increased the energy demands to provide the required services. Hence, there is a need for the development of efficient, clean, and sustainable energy sources rather than fossil fuels. Renewable energy sources are a suitable alternative to fossil fuels due to the tight environmental regulations and depletion of natural fossil fuels (Sarwar *et al.*, 2017). Polymeric nanocomposites also find applications in generating green and environment-friendly energy. Some techniques have been developed based on the PNCs for the conservation and storage of electrochemical energy such as fuel cells (Kim *et al.*, 2015), solar cells (Lasrado *et al.*, 2020), lithium-ion batteries (LIBs) (Masoud *et al.*, 2020), and supercapacitors (Sahoo, 2017).

Fuel cells are the devices that convert stored chemical energy into fuels like hydrogen, methanol, ethanol, and formic acid (Hossain and Hoque, 2018). They are known to have the merit to be great alternatives to fossil fuels since they are highly efficient and do not produce any pollution such as SO_x , NO_x , and CO_2 in comparison with coal combustion engines. Fuel cells are classified into five different types based on the mode of operation, operation temperature, and nature of electrolyte. Among them, polymer electrolyte membrane (PEM) is the most promising for the generation of power for portable devices, automotive, and stationary applications (Mehta and Cooper, 2003). Different types of PNCs have been explored to be used to enhance the performance of conventional proton conducting membranes such as Nafion, sulfonated poly (ether ether ketone) (SPEEK), poly (ether sulfone) (PES), and poly(benzimidazole) (PBI) (Chen *et al.*, 2012). They possess superior properties such as high proton conductivity and excellent thermal and mechanical stability at low humidity and high temperature (Luo *et al.*, 2016).

CNT and graphene and its derivatives, as nanofillers, can also be used to boost performance and reduce the cost of polymer solar cells (PSCs) by enhancing their different constituents, such as glass electrodes, liquid electrolytes, and catalyst layer (Saleh *et al.*, 2020). Another outstanding photovoltaic technology is dye-sensitized solar cells (DSSCs), which is a low-cost and high-efficiency method for the generation of energy. The only drawbacks of this method are the presence of expensive and brittle fluorine-doped tin oxide glass coated with a platinum film cathode and stability issues due to leakage and volatilization of organic solvents. Rehman *et al.* recently synthesized a polyvinyl acetate (PVAc)/graphene nanocomposite-based gel electrolyte for the first time using the in-situ intercalative polymerization technique to enhance the efficiency of the solar cells. Their results showed an increase in the photovoltaic conversion efficiencies (PCEs) from 4.35% to 4.57% (Rehman *et al.*, 2020). In another study, Bayram *et al.* produced graphene/polyaniline nanocomposite thin films as counter electrode materials to be used in place of platinum (Pt)-counter electrode. Their results confirmed the successful replacement of PNCs with the platinum electrode in dye-sensitized solar cells (Bayram *et al.*, 2020).

Another popular application of PNCs is in LIBs. Having high voltage, huge power, low toxicity, and long life cycle has made the LIBs more popular for their application as a rechargeable battery in recent years (Ding *et al.*, 2014). Intrinsically conductive polymers (ICPs) have attracted significant research efforts to improve the performances of conventional LIB electrode materials. The electroactive organic functional groups in the ICPs have faster redox reaction kinetics than conventional inorganic LIB electrode materials (Yang *et al.*, 2015). Arya and Sharma prepared a PNC based on blend PEO-PVC, LiPF_6 as salt, and modified montmorillonite (MMMT) as nanoclay by solution cast method for application in LIBs. According to their results, an increase in the fraction of free anions, thermal stability (up to 300 °C), ion transference number (~ 1), and voltage stability window of ~ 5 V was observed with the addition of clay into the polymer matrix for a LIB (Arya and Sharma, 2020).

In another application, PNCs can be used in supercapacitors. Among different techniques for energy storage such as fuel cells, solar cells, LIBs, and supercapacitors, the supercapacitors possess the advantage of high-power density due to the fast-electrical energy storage and discharge capability. The higher specific capacitance value of the conducting polymer nanostructures makes them an alternate in the development of the next-generation energy storage devices (Mishra and Valodkar, 2017; Wang and Zhu, 2011). Khan *et al.* prepared an electrode material based on composites of polyaniline, graphite nanoplatelets (GNP), and polystyrene matrix (PANI/GnP/PS). Their results showed that PANI/GnP/PS nanocomposite exhibited a lower reduction (32%) in the specific capacitance after 1600 charge-discharge cycles compared to other electrodes, demonstrating it as an ideal electrode in supercapacitors (Khan *et al.*, 2020).

PNCs also receive a widespread attraction for application in high-voltage cable insulations. Paramane *et al.* prepared a cross-linked polyethylene (XLPE)/MgO nanocomposite material and investigated its performance for the insulation of commercial 320 kV high-voltage direct-current (HVDC). Based on their observations, the direct-current (DC) breakdown strength of the prepared nanocomposite was improved by 20% due to the higher deep trap density and lower charge carrier mobility. They also studied the effect of thermal aging on the insulation performance of the PNC. The thermally aged nanocomposite showed greater restraint against the degradation of its properties. The DC breakdown strength also decreased after thermal aging by 38% and 20% in the pure XLPE and its nanocomposite, respectively (Paramane *et al.*, 2020). The successful application of PNCs for high voltage insulation has been also confirmed by other researchers (Li *et al.*, 2020; Yu *et al.*, 2020; Lau and M. Piah, 2011).

Corrosion Protection Applications

Corrosion which usually involves the oxidation of the metal and the reduction of oxygen, protons, and/or water, is a global challenge with a cost of \$2.5 trillion annually worldwide (Umoren and Solomon, 2019). Corrosion protection has become an issue of great concern in the modern metallic finishing industry (Yang *et al.*, 2015). Different strategies have been employed to combat corrosion, among which the use of corrosion inhibitors and coatings are the most popular ones. However, common organic inhibitors cannot provide long-term corrosion protection because of their brittle structure and hydrolytic degradation during exposure to a corrosive environment. Research has shown that the introduction of inorganic nanoscale materials into the polymer matrices could remarkably increase the corrosion inhibition efficiency (Umoren and Madhankumar, 2016; Salehoun *et al.*, 2017; Solomon *et al.*, 2017). Different types of nano-sized fillers have been used in different researches to improve the barrier protection of polymer coatings and reduce the permeability of aggressive species into the coatings, such as inorganic nanomaterials (Atta *et al.*, 2019), layered doubled hydroxides (Olya *et al.*, 2020), clays (Davoodi *et al.*, 2020), and graphene-based nanomaterial (Javidparvar *et al.*, 2020). Pourhashem *et al.* demonstrated that incorporation of inorganic nanomaterials including metal and metal oxides, nano-glass flakes, nitrides, and borides, and nano-calcium carbonate into a polymer matrix produces

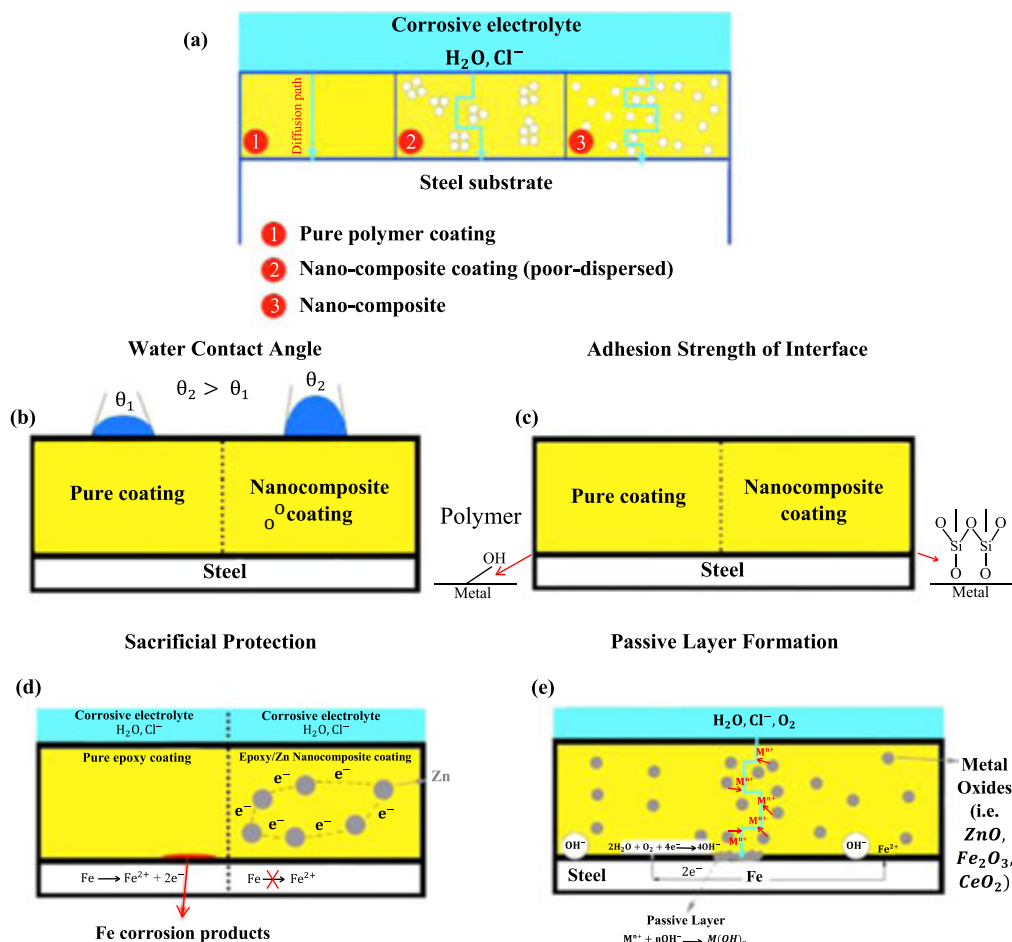


Fig. 4 Corrosion protection mechanism of polymer coatings containing inorganic nanomaterials: (a) barrier performance; (b) increasing water contact angle; (c) increasing adhesion strength at coating/metal interface; (d) sacrificial protection; and (e) passive layer formation. Reproduced from Pourhashem, S. Saba, F., Duan, J., *et al.*, 2020. Polymer/inorganic nanocomposite coatings with superior corrosion protection performance: A review. *Journal of Industrial and Engineering Chemistry* 88, 29–57.

corrosion-resistant coatings. On the other hand, the other aspects of coatings including thermal stability, UV resistance, weathering resistance, mechanical performance, and hydrophobic property can be improved along with the corrosion resistance (Fig. 4) (Pourhashem *et al.*, 2020).

Ballistic, Aerospace, and Automobile Applications

Another application of PNCs is in the automobile and aerospace industry. The size scale, aspect ratio, and properties of nanofillers such as nanotubes provide great advantages for PNCs to be used for different applications such as electrostatically dissipative materials, advanced materials with combined stiffness and strength for application in aerospace or sporting goods, composite mirrors, and automotive parts that require electrostatic painting and automotive components with enhanced mechanical properties (Sahoo and Tripathy, 2017). Moreover, a 10% reduction in automobile weight can improve fuel efficiency by 6–8%, so this industry needs to develop lightweight materials. Toyota Motor Company was the first who pioneered the first practical example of polymeric nanocomposite for automobile applications (Garces *et al.*, 2000). Besides, Japan developed a reinforced elastomer comprising elastomer-based materials (including natural rubber, butadiene rubber copolymers, and polychloroprene rubbers) and a modified clay PNC, using as the engine cover in Mitsubishi vehicles (Carter *et al.*, 1947). Ford Motor Company has indicated that weight reduction is a key part of its strategy to improve fuel economy by 40% by the year 2020. They have planned the company's goal to reduce vehicle weight as much as 750 lbs (340 kg), depending on the model, without compromising safety. To achieve the goal, one path that Ford scientists are taking is the replacement of metal with PNCs (Stewart, 2009).

The mechanical properties of the PNCs can be drastically enhanced, by a little increment in the material cost. This enables them to be cost-competitive in comparison with traditional polymers and finally, replace the metal and glass in the vehicle. As a result, the automotive industry is enabled to capture a leadership position in high-quality, fuel-efficient, fast production, and durable vehicles (Garces *et al.*, 2000).

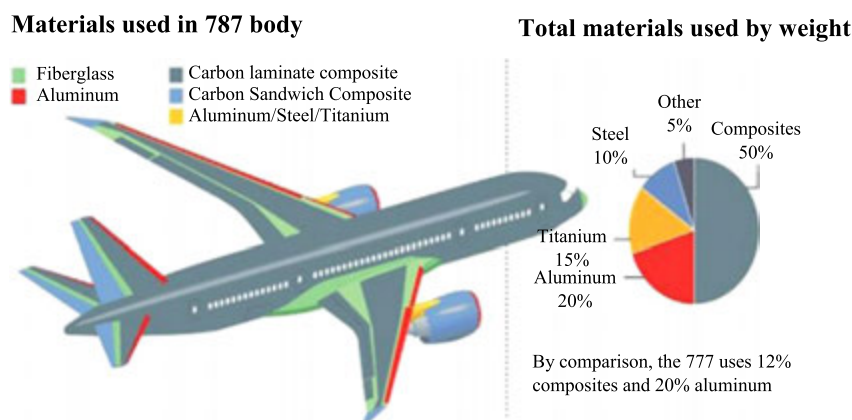


Fig. 5 General application of composites with respect to other materials in commercial airplanes. Reproduced from Behera, A., Mallick, P., 2020. Chapter 20 – Application of nanofibers in aerospace industry. In: Han, B., Sharma, S., Nguyen, T.A., Longbiao, L., Subrahmanya Bhat, K. (Eds.), *Fiber-Reinforced Nanocomposites: Fundamentals and Applications*, Elsevier. pp. 449–457.

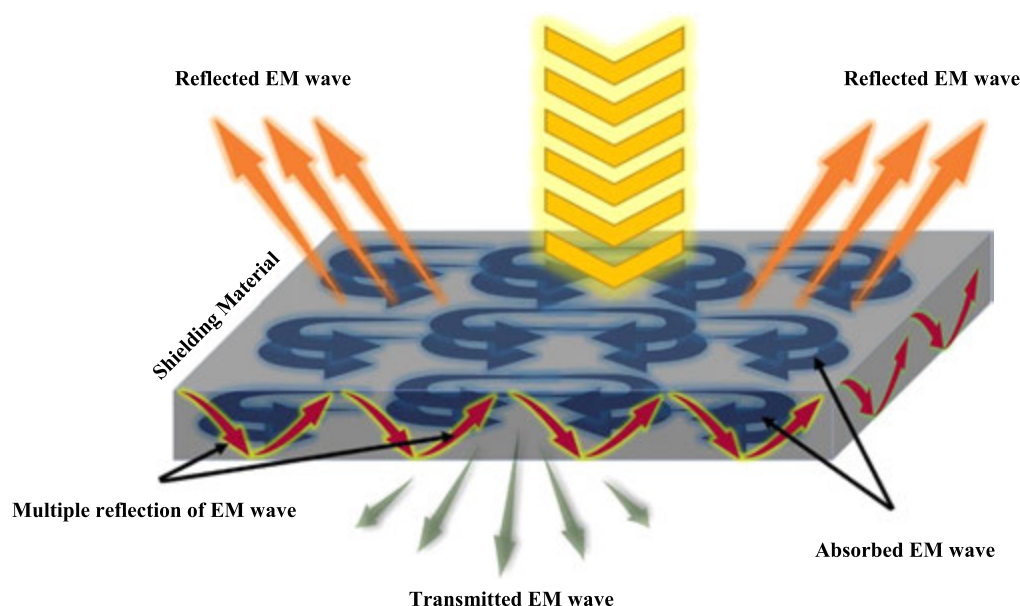


Fig. 6 The general processes of an incident EM wave through an EM absorption material. Reproduced from Rani, P., Ahamed, M.B., Deshmukh, K., 2020. Significantly enhanced electromagnetic interference shielding effectiveness of montmorillonite nanoclay and copper oxide nanoparticles based polyvinylchloride nanocomposites. *Polymer Testing* 91, 106744.

For aircraft flying at high altitudes, some properties such as low solar absorption, radiation resistance, high thermal emissivity, resistance to corrosion, and electrical conductivity are important (Rathod *et al.*, 2017). The addition of different concentrations of nanofillers such as fibers, whiskers, platelets, and CNTs to the composites, the previous properties could be usually fulfilled. Depending upon the matrix and nanofiller, PNCs can be used in the airplane turbine engine (for protection of turbine blades against high-speed particle impact) (Lee *et al.*, 2012), fuselage (for weight and cost reduction and corrosion protection), horizontal and vertical stabilizers, and nose (Behera and Mallick, 2020). Fig. 5 illustrates different types of materials including composites used in the structure of commercial airplanes with a comparison between their compositional percentage.

Electromagnetic interference (EMI) shielding is another important application of PNC. EMI shields can be used to protect humans or devices from being harmed or something such as airplanes from being detected. PNCs are ideal EM wave absorbers due to their relatively lightweight, thin thickness, high EM absorption, tunable absorption characteristics, broad width, etc. (Abbasi *et al.*, 2019). Fig. 6 displays the general process of an incident EM wave through an EM absorption material.

Among different types of polymer matrices, Ling *et al.* reported a facile approach to produce lightweight microcellular polyetherimide (PEI)/graphene nanocomposite foams with a density of about 0.3 g/cm^3 by a phase separation process. They demonstrated that PEI/graphene nanocomposite foams exhibited well-defined thermal insulation and tensile properties. Furthermore, they reported that the specific EMI shielding effectiveness of microcellular PEI/graphene foams was $36.1 \text{ dB/(g/cm}^3\text{)}$ and

44.1 dB/(g/cm³) for 7 wt% and 10 wt% loading, respectively, which was about 2.2 and 2.5 times higher than the unfoamed counterparts (Ling *et al.*, 2013).

Singh and Kulkarni presented the application of the nanocomposites based on different transition metal oxides like iron oxide (Fe₂O₃), zinc oxide (ZnO), silicon dioxide (SiO₂), zirconium dioxide (ZrO₂), and titanium dioxide (TiO₂) in the Polyvinyl alcohol (PVA) matrix for their suitability as EMI shielding materials in the frequency range of 4–8 GHz (C-band) and 8–12 GHz (X-band). They prepared different concentrations of nano-oxides from 0.1, 0.5, 1.0, 5.0, and 10.0 wt% in a PVA matrix and synthesized the PNCs via the solvent casting method. Based on their experimental results, the reflectivity decreases by increasing the nano-oxides concentration and the minimum reflectivity values of PVA–SiO₂, PVA–Fe₂O₃, PVA–ZnO, PVA–TiO₂, and PVA–ZrO₂ at 10 wt% concentration of nano-oxides were –41.9 dB (10.4 GHz), –38.85 dB (10.4 GHz), –33.65 dB (10.4 GHz), –32.90 dB (9.76 GHz), and –24.90 dB (11.0 GHz), respectively. All of the composites exhibit very good thermal stability and high mechanical strength, making them more promising for EMI shielding applications (Singh and Kulkarni, 2014).

Ultraviolet Protection Applications

UV light is known to be harmful to all living beings. Many different methods have been developed to protect against UV radiations such as sunglasses, sunscreen lotions/creams, window protectors, and clothes. Another cost-effective method to provide protection against UV-rays is UV-shielding PNCs. However, most traditional UV protectors provide good UV-block performance, they suffer from photodegradation, migration, and aggregation. Several researchers have confirmed the high UV-shielding performance of different bio-inspired PNCs such as dopamine-melanin solid nanoparticles (Dpa-s NPs) and hollow nanoparticles (Dpa-h NPs) (Wang *et al.*, 2017), polyacrylonitrile (PAN)/multi-walled carbon nanotubes (MWCNTs) composite (Nasouri, *et al.*, 2020), and composite-based polyethylene terephthalate (PET) (Bouazizi *et al.*, 2020).

Sensors Applications

In recent years, polymer-nanocomposites have been used for sensing applications such as gas sensors, biosensors, and chemical sensors. Different types of nanofillers can be employed for this purpose including metal oxide nanowires, CNTs, nanoscale gold, silver, nickel, copper, platinum, and palladium particles (Saleh *et al.*, 2020). The resulting PNC sensors are designed to be sensitive to the pH changes, possess an affinity for organic molecules and inorganic ions, and monitor the existing pathogens. In some researches, their applicability was successfully determined in the detection of free chlorine, ferricyanide, ammonia and amines, bisphenol A, ibuprofen, and (chemical oxygen demand/dissolved oxygen) COD/DO levels in aqueous systems (Cheng *et al.*, 2016; Muñoz *et al.*, 2015; Motoc *et al.*, 2013; Akharam *et al.*, 2018).

Smart Polymer Nanocomposites Applications

Recent advances in PNCs have led to the development of smart PNCs with scientific and industrial potential in various application areas such as shape memory, self-healing, self-sensing, self-cleaning, and energy harvesting (Idumah, 2019). Smart PNCs are used for different purposes such as sensors/actuators (Kumar *et al.*, 2020), wearable electronics, smart textiles (Elhalawany *et al.*, 2020), drug delivery (Zhang, *et al.*, 2013), stretchable electronics, and aerospace applications (Zhu *et al.*, 2019).

A smart textile was fabricated based on the conjugated polymers by Lee *et al.*, by assembling a conjugated polymer with a fatty acid via an emulsion process and distributing the fiber nanoparticles in a polyacrylonitrile matrix. Based on their results, the textiles showed an excellent photothermal temperature from 25°C to 55°C in 10 min, because of efficient photothermal conversion under white light irradiation. Besides, the smart PNC textile showed better antimicrobial activity and strong colorfastness than Ag nanofillers, demonstrating their practical application in the textile industry (Lee *et al.*, 2019).

Wan and Chen synthesized a smart PNC coating from waterborne polyurethane and graphene oxide (GO). They prepared a series of self-healing waterborne polyurethane/GO nanocomposites with different concentrations using the solution blending method. Their results showed a 22%–47% enhancement in the tensile strengths of the nanocomposites compared with that of neat waterborne polyurethane. On the other hand, the sample containing 0.5 wt% GO showed the best self-healing performance, as obvious in Fig. 7 (Wan and Chen, 2018).

Adhesive Applications

The first reports regarding the synthesis of the first adhesives date back to 1920. Since then many efforts have been done to develop synthetic polymers as adhesives. In recent years, many studies have shown that the incorporation of nanoparticles into polymeric adhesives enhances their performance (Cudjoe *et al.*, 2018). Luo *et al.* studied the effect of the addition of nanoparticles into thermoplastic polyurethane adhesives (TPU). They found that the use of silver flakes and CNTs as nanofiller enhanced the mechanical, electrical, and thermal properties of the nanocomposites. Moreover, the electrical conductivity was increased by 86.6% after the addition of 4.5 wt% CNT into the 50 wt% Ag TPU adhesives (Luo *et al.*, 2016).

Khalina *et al.* studied the preparation of a pressure-sensitive adhesive, comprising of a definite ratio of 2-ethylhexyl acrylate/acrylic acid/methyl methacrylate (2-EHA/AA/MMA) monomers and nanosilica fillers. They found that the addition of 0%–4%

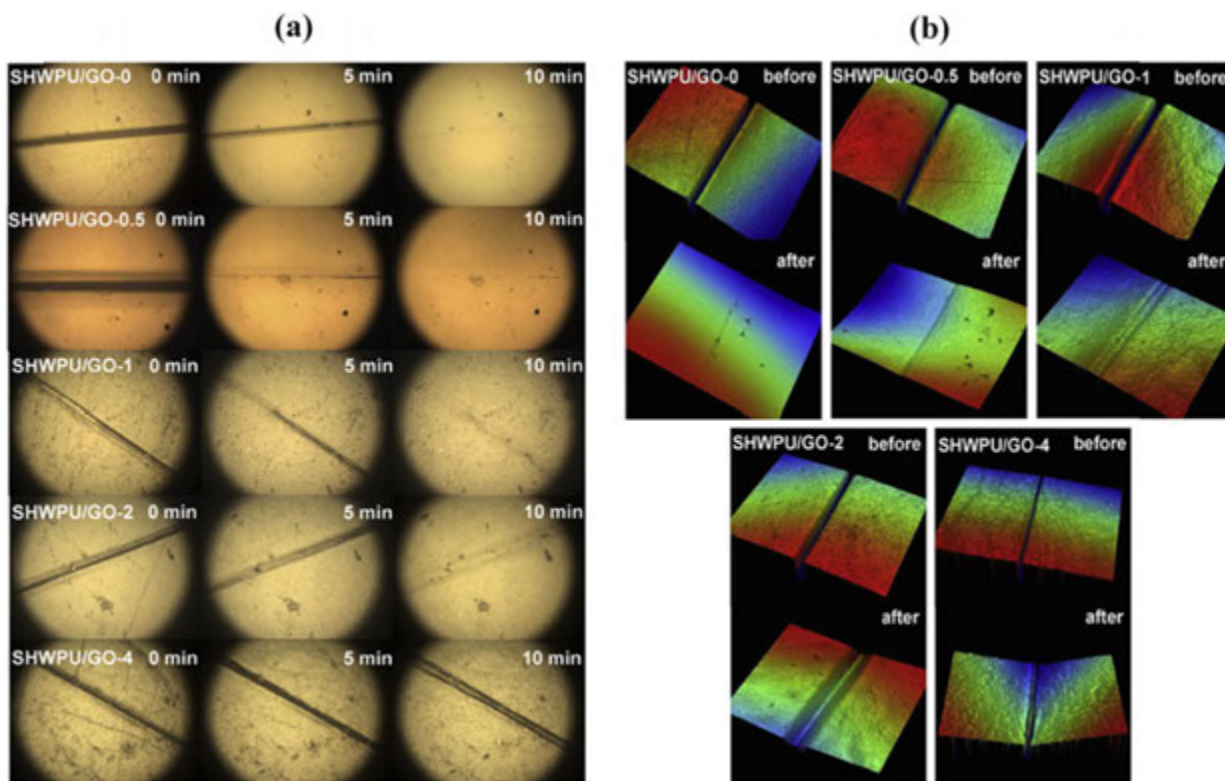


Fig. 7 (a) Microscope images of cracked SHWPU/GO films at different healing time and (b) Surfaces topography images of cracked SHWPU/GO films before and after healing at 70 °C for 10 min. Reproduced from Wan, T., Chen, D., 2018. Mechanical enhancement of self-healing waterborne polyurethane by graphene oxide. *Progress in Organic Coatings* 121, 73–79.

nanosilica increases viscosity, elastic modulus, and loss modulus. Based on the analysis of adhesion properties such as tack, peel, and shear strength for the nanocomposite films containing 4 wt% of nanosilica, a significant improvement of up to 300% was observed in the tack resistance. (Khalina *et al.*, 2015).

Flame Retardant Polymer Nanocomposites

Despite the outstanding properties of PNCs such as lightweight, superior mechanical properties, high chemical stability, corrosion resistance, easy processing procedure, and high specific strength, they suffer from intrinsic flammability, arises from their chemical structures and organic compositions. Fig. 8 represents a schematic for a typical combustion process of polymers. This property significantly restricted the practical applications of PNCs in electronics, building, automotive, transport, textile, and aerospace fields. To overcome this limitation, many researchers have addressed the synthesis of flame retardant PNCs (He *et al.*, 2020; Wang *et al.*, 2011; Kong *et al.*, 2017; Xu *et al.*, 2020; Higginbotham *et al.*, 2009; Morgan and Wilkie, 2007). The presence of nanoparticles can reduce the flammability of PNCs by decreasing the heat release rate and increasing the ability to flame-out and auto-extinguish (Morgan and Wilkie, 2007). Higginbotham *et al.* developed a GO PNC at 1, 5, and 10 wt% GO with polycarbonate (PC), acrylonitrile butadiene styrene (ABS), and high-impact polystyrene (HIPS), to study the influence of nanoparticle addition on the flammability reduction of PNCs. They observed an increase in the storage modulus by increasing the GO loading. Besides, the addition of GO reduced the total/peak heat release rates in all systems, and GO-PC composites demonstrated very fast self-extinguishing times in vertical open flame tests, which are important to some regulatory fire safety applications (Higginbotham *et al.*, 2009). Their work revealed that GO nanoparticles are promising additives for the fabrication of flame-retardant PNCs.

Kong *et al.* studied the improvement in flame retardant properties of intumescent flame retardant/polypropylene (IFR/PP) through the synergistic effect of organic montmorillonite intercalation cobalt hydroxides (Co-OMMT) modified by acidified chitosan. They fabricated the Co-OMMT/IFR/PP nanocomposites via the melt blending method. The results of limiting oxygen index (LOI) and vertical burning (UL-94) tests indicated that IFR/PP composites only reached a V-2 rating with the LOI value of 26.5%. An addition of 4 wt% of Co-OMMT nanoparticles into the IFR/PP matrix resulted in a flame-retardant nanocomposite that passed UL-94V-0 rating with a higher LOI value of 32.1%. Furthermore, based on the results of CC tests, the values of peak heat release rate (PHRR), total heat release (THR), and peak smoke production rate (PSPR) of 4 wt% Co-OMMT/IFR/PP nanocomposites decreased by 33.7%, 11.8%, and 16.7%, respectively, compared to that of IFR/PP. This may be due to the formation of

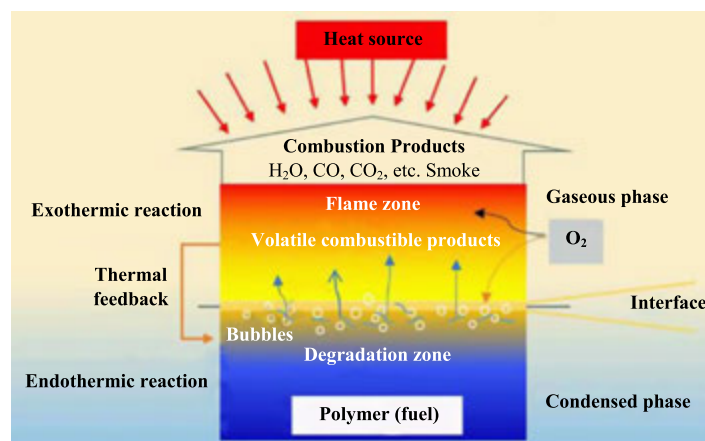


Fig. 8 Schematic representation for a typical combustion process of polymers. Reproduced from He, W., Song, P., Yu, B., Fang, Z., Wang, H., 2020. Flame retardant polymeric nanocomposites through the combination of nanomaterials and conventional flame retardants. *Progress in Materials Science* 114, 100687.

the compact char protection layers in the condensed phase during burning, which efficiently inhibited the heat and mass transmission and prevented organic degradation volatiles from getting into the gas phase (Kong *et al.*, 2017).

Wang and co-workers reported the flame-retardant systems consisting of nano-ZrO₂ and triphenyl phosphate (TPP) for PMMA. The results of the CC test, TGA, Raman spectra, SEM, and X-ray photoelectron spectroscopy (XPS) confirmed the synergistic effect of nano-ZrO₂ with TPP for PMMA polymer matrix. A reduction in the peak heat release rate and an increment in the thermal stability was observed by increasing the content of nano-ZrO₂, confirming the flame retardancy of the obtained PNC material (Wang *et al.*, 2011).

Conclusion

Nowadays, with the increase in industrialization, polymers have found application in many fields of engineering from automobiles through biomedical applications, energy-related applications, coatings and corrosion protection, ballistic and aerospace applications, UV protection, sensors, and adhesive applications. Lack of some features such as flammability, conductivity, biocompatibility, and good mechanical properties has limited their application for certain practical purposes. Adding nanoparticles into the polymer structure leads to the formation of PNCs, which to some extent resolves the issues with single polymers. In this article, different types of nanocomposites and their properties, advantages, and disadvantages are first described with a high focus on the PNCs. Then a detailed explanation is given to describe their characterization techniques including structural analysis, thermal properties, mechanical properties, and electrical properties. Finally, the various industrial applications of the PNCs such as biomedical and tissue engineering applications, energy-related applications, corrosion protection applications, ballistic, aerospace, and automobile applications, UV protection applications, sensors applications, smart PNCs applications, adhesive applications, and flame-retardant PNCs are described in detail.

References

- Abbasi, H., Antunes, M., Velasco, J.I., 2019. Recent advances in carbon-based polymer nanocomposites for electromagnetic interference shielding. *Progress in Materials Science* 103, 319–373.
- Abhilash, V., Rajender, N., Suresh, K., 2016. Chapter 14 – X-ray diffraction spectroscopy of polymer nanocomposites. In: Thomas, S., Rouxel, D., Ponnamm, D. (Eds.), *Spectroscopy of Polymer Nanocomposites*. Elsevier, pp. 410–451.
- Akhrame, M.O., Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I., Oputu, O.U., 2018. Polymeric nanocomposites (pncs) for wastewater remediation: An overview. *Polymer-Plastics Technology and Engineering* 57, 1801–1827.
- Alexandre, M., Dubois, P., 2000. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Materials Science and Engineering: R Reports* 28, 1–63.
- Allaoui, A., Bai, S., Cheng, H.-M., Bai, J., 2002. Mechanical and electrical properties of a mwnt/epoxy composite. *Composites Science and Technology* 62, 1993–1998.
- Anaghi, A., Baitukha, A., Debiemme-Chouvy, C., *et al.*, 2019. Nanocomposite coatings based on graphene and siloxane polymers deposited by atmospheric pressure plasma. Application to Corrosion Protection of steel. *Surface and Coatings Technology* 377, 124928.
- Ansari, M.O., Khan, M.M., Ansari, S.A., Cho, M.H., 2015. Electrically conductive polyaniline sensitized defective-TiO₂ for improved visible light photocatalytic and photoelectrochemical performance: A synergistic effect. *New Journal of Chemistry* 39, 8381–8388.
- Arya, A., Sharma, A.L., 2020. Investigation on enhancement of electrical, dielectric and ion transport properties of nanoclay-based blend polymer nanocomposites. *Polymer Bulletin* 77, 2965–2999.
- Atta, A.M., Mohamed, N.H., Rostom, M., Al-Lohedan, H.A., Abdullah, M.M.S., 2019. New hydrophobic silica nanoparticles capped with petroleum paraffin wax embedded in epoxy networks as multifunctional steel epoxy coatings. *Progress in Organic Coatings* 128, 99–111.

- Baeza, G.P., Genix, A.-C., Paupy-Peyronnet, N., *et al.*, 2016. Revealing nanocomposite filler structures by swelling and small-angle x-ray scattering. *Faraday Discussions* 186, 295–309.
- Balint, R., Cassidy, N.J., Cartmell, S.H., 2014. Conductive polymers: Towards a smart biomaterial for tissue engineering. *Acta Biomaterialia* 10, 2341–2353.
- Bandaru, P.R., 2007. Electrical properties and applications of carbon nanotube structures. *Journal of Nanoscience and Nanotechnology* 7, 1239–1267.
- Bandyopadhyay, S., Samudrala, S., Bhowmick, A., Gupta, S., 2008. Applications of atomic force microscope (AFM) in the field of nanomaterials and nanocomposites. In: Seal, S. (Ed.), *Functional Nanostructures: Processing, Characterization, and Applications*. Springer, pp. 504–568.
- Bayram, O., Igman, E., Guney, H., *et al.*, 2020. Graphene/polyaniline nanocomposite as platinum-free counter electrode material for dye-sensitized solar cell: Its fabrication and photovoltaic performance. *Journal of Materials Science: Materials in Electronics* 31, 10288–10297.
- Behera, A., Mallick, P., 2020. Chapter 20 – Application of nanofibers in aerospace industry. In: Han, B., Sharma, S., Nguyen, T.A., Longbiao, L., Subrahmanya Bhat, K. (Eds.), *Fiber-Reinforced Nanocomposites: Fundamentals and Applications*. Elsevier, pp. 449–457.
- Berthomieu, C., Hienerwadel, R., 2009. Fourier transform infrared (ftir) spectroscopy. *Photosynthesis Research* 101, 157–170.
- Bharathidasan, T., Sathiyarayanan, S., 2020. Self-replenishing superhydrophobic durable polymeric nanocomposite coatings for heat exchanger channels in thermal management applications. *Progress in Organic Coatings* 148, 105828.
- Bhattacharya, M., 2016. Polymer nanocomposites – A comparison between carbon nanotubes, graphene, and clay as nanofillers. *Materials* 9, 262.
- Bhattacharya, S., Kamal, M., Gupta, R., 2007. Polymeric nanocomposites theory and practice. Carl Hanser Publishers/Hanser Gardner Publications. (Munich/Cincinnati).
- Bishnoi, A., Kumar, S., Joshi, N., 2017. Chapter 9 – Wide-angle x-ray diffraction (WAXRD): Technique for characterization of nanomaterials and polymer nanocomposites. In: Thomas, S., Thomas, R., Zachariah, A.K., Mishra, R.K. (Eds.), *Microscopy methods in nanomaterials characterization*. Elsevier, pp. 313–337.
- Bouazizi, N., Abed, A., Giraud, S., *et al.*, 2020. Development of new composite fibers with excellent uv radiation protection. *Physica E: Low-dimensional Systems and Nanostructures* 118, 113905.
- Braga, P.C., Ricci, D., 2004. Atomic Force Microscopy: Biomedical Methods and Applications. Springer Science & Business Media.
- Burdock, G.A., 2007. Safety assessment of hydroxypropyl methylcellulose as a food ingredient. *Food and Chemical Toxicology* 45, 2341–2351.
- Burgaz, E., 2016. Thermomechanical analysis of polymer nanocomposites. In: Huang, X., Zhi, C. (Eds.), *Polymer Nanocomposites*. Springer, pp. 191–242.
- Camargo, P.H.C., Satyanarayana, K.G., Wypych, F., 2009. Nanocomposites: Synthesis, structure, properties and new application opportunities. *Materials Research* 12, 1–39.
- Candan, Z., Gardner, D.J., Shaler, S.M., 2016. Dynamic mechanical thermal analysis (DMTA) of cellulose nanofibril/nanoclay/pmda nanocomposites. *Composites Part B: Engineering* 90, 126–132.
- Carter, L.W., Hendricks, J.G., Bolley, D.S., 1947. Elastomer reinforced with a modified clay, U.S.P.a.T.-US2531396A, United States.
- Chattopadhyay, D.K., Webster, D.C., 2009. Thermal stability and flame retardancy of polyurethanes. *Progress in Polymer Science* 34, 1068–1133.
- Chauhan, S.S., Singh, B.P., Malik, R.S., Verma, P., Choudhary, V., 2018. Detailed dynamic mechanical analysis of thermomechanically stable melt-processed PEK–MWCNT nanocomposites. *Polymer Composites* 39, 2587–2596.
- Chen, J., Liu, B., Gao, X., Xu, D., 2018. A review of the interfacial characteristics of polymer nanocomposites containing carbon nanotubes. *RSC Advances* 8, 28048–28085.
- Chen, J., Guo, Q., Li, D., Tong, J., Li, X., 2012. Properties improvement of speak based proton exchange membranes by doping of ionic liquids and Y_2O_3 . *Progress in Natural Science: Materials International* 22, 26–30.
- Cheng, C., Wang, S., Wu, J., *et al.*, 2016. Bisphenol A sensors on polyimide fabricated by laser direct writing for onsite river water monitoring at attomolar concentration. *ACS Applied Materials & Interfaces* 8, 17784–17792.
- Corcione, C.E., Frigione, M., 2012. Characterization of nanocomposites by thermal analysis. *Materials* 5, 2960–2980.
- Cser, F., Bhattacharya, S., 2003. Study of the orientation and the degree of exfoliation of nanoparticles in poly (ethylene-vinyl acetate) nanocomposites. *Journal of Applied Polymer Science* 90, 3026–3031.
- Cudjoe, E., Herbert, K.M., Rowan, S.J., 2018. Strong, rebondable, dynamic cross-linked cellulose nanocrystal polymer nanocomposite adhesives. *ACS Applied Materials & Interfaces* 10, 30723–30731.
- Cui, Y., Kumar, S., Rao Kona, B., van Houcke, D., 2015. Gas barrier properties of polymer/clay nanocomposites. *RSC Advances* 5, 63669–63690.
- Davoodi, M., Ghasemi, E., Ramezanzadeh, B., Mahdavian, M., 2020. Designing a zinc-encapsulated feldspar as a unique rock-forming tectosilicate nanocontainer in the epoxy coating: improving the robust barrier and self-healing anti-corrosion properties. *Construction and Building Materials* 243, 118215.
- Demchenko, V., Riabov, S., 2017. X-ray study of structural formation and thermomechanical properties of silver-containing polymer nanocomposites. *Nanoscale Research Letters* 12, 1–6.
- Demchenko, V., Riabov, S., Rybalchenko, N., *et al.*, 2017. X-ray study of structural formation, thermomechanical and antimicrobial properties of copper-containing polymer nanocomposites obtained by the thermal reduction method. *European Polymer Journal* 96, 326–336.
- Din, S.H., 2019. Nano-composites and their applications: A review. *Characterization and Application of Nanomaterials* 2.
- Ding, K., Gu, H., Zheng, C., *et al.*, 2014. Octagonal prism shaped lithium iron phosphate composite particles as positive electrode materials for rechargeable lithium-ion battery. *Electrochimica Acta* 146, 585–590.
- Drzeżdżon, J., Jacewicz, D., Sielicka, A., Chmurzyński, L., 2019. A review of new approaches to analytical methods to determine the structure and morphology of polymers. *Trends in Analytical Chemistry* 118, 470–476.
- Duncan, T.V., 2011. Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. *Journal of Colloid and Interface Science* 363, 1–24.
- Elhalawany, N., El-Naggar, M.E., Elsayed, A., *et al.*, 2020. Polyaniline/zinc/aluminum nanocomposites for multifunctional smart cotton fabrics. *Materials Chemistry and Physics* 249, 123210.
- Feldman, D., 2019. Polymers and polymer nanocomposites for cancer therapy. *Applied Sciences* 9, 3899.
- Fu, H.-K., Kuo, S.-W., Yeh, D.-R., Chang, F.-C., 2008. Properties enhancement of PS nanocomposites through the POSS surfactants. *Journal of Nanomaterials* 2008.
- Garces, J.M., Moll, D.J., Bicerano, J., Fibiger, R., McLeod, D.G., 2000. Polymeric nanocomposites for automotive applications. *Advanced Materials* 12, 1835–1839.
- X-ray scattering applied to the analysis of carbon nanotubes. *Óptica Pura Aplicada* 40 (2).
- Goyal, R.K., 2017. *Nanomaterials and Nanocomposites: Synthesis, Properties, Characterization Techniques, and Applications*. CRC Press.
- Haghighi, M., Ansari, R., Hassanzadeh-Aghdam, M., Nankali, M., 2019. Analytical formulation for electrical conductivity and percolation threshold of epoxy multiscale nanocomposites reinforced with chopped carbon fibers and wavy carbon nanotubes considering tunneling resistivity. *Composites Part A: Applied Science and Manufacturing* 126, 105616.
- Hajiali, H., Karbasi, S., Hosseinalipour, M., Rezaie, H.R., 2010. Preparation of a novel biodegradable nanocomposite scaffold based on poly (3-hydroxybutyrate)/bioglass nanoparticles for bone tissue engineering. *Journal of Materials Science: Materials in Medicine* 21, 2125–2132.
- Hanna, A., Nour, M., Souaya, E., Abdelmoaty, A., 2018. Studies on the flammability of polypropylene/ammonium polyphosphate and montmorillonite by using the cone calorimeter test. *Open Chemistry* 16, 108–115.
- Hashemi, R., Weng, G.J., 2016. A theoretical treatment of graphene nanocomposites with percolation threshold, tunneling-assisted conductivity and microcapacitor effect in ac and dc electrical settings. *Carbon* 96, 474–490.
- He, W., Song, P., Yu, B., Fang, Z., Wang, H., 2020. Flame retardant polymeric nanocomposites through the combination of nanomaterials and conventional flame retardants. *Progress in Materials Science* 114, 100687.
- Herron, N., Thorn, D.L., 1998. Nanoparticles: Uses and relationships to molecular cluster compounds. *Advanced Materials* 10, 1173–1184.

- Higginbotham, A.L., Lomeda, J.R., Morgan, A.B., Tour, J.M., 2009. Graphite oxide flame-retardant polymer nanocomposites. *ACS Applied Materials & Interfaces* 1 (10), 2256–2261.
- Hossain, S.K.S., Hoque, M.E., 2018. Chapter 9 – Polymer nanocomposite materials in energy storage: Properties and applications. In: Jawaid, M., Khan, M.M. (Eds.), *Polymer-Based Nanocomposites for Energy and Environmental Applications*. Woodhead Publishing, pp. 239–282.
- Hosseini, S.H., Noushin Ezzati, S., Askari, M., 2015. Synthesis, characterization and x-ray shielding properties of polypyrrole/lead nanocomposites. *Polymers for Advanced Technologies* 26, 561–568.
- Idumah, C.I., 2019. Recent Advancements in Self-healing Polymers, Polymer Blends, and Nanocomposites. *Polymers and Polymer Composites* 1, 1–13.
- Javidparvar, A.A., Naderi, R., Ramezanzadeh, B., 2020. L-cysteine reduced/functionalized graphene oxide application as a smart/control release nanocarrier of sustainable cerium ions for epoxy coating anti-corrosion properties improvement. *Journal of Hazardous Materials* 389, 122135.
- Jayanarayanan, K., Rasana, N., Mishra, R.K., 2017. Dynamic mechanical thermal analysis of polymer nanocomposites. In *Thermal and Rheological Measurement Techniques for Nanomaterials Characterization*. Elsevier, pp. 123–157.
- Jeon, I.-Y., Baek, J.-B., 2010. Nanocomposites derived from polymers and inorganic nanoparticles. *Materials* 3, 3654–3674.
- Jordan, J., Jacob, K.I., Tannenbaum, R., Sharaf, M.A., Jasiuk, I., 2005. Experimental trends in polymer nanocomposites – A review. *Materials Science and Engineering A* 393, 1–11.
- Joshi, P., Kumar, D., 2018. Chapter 17 – The role of polymer nanocomposite-based membranes for environmental remediation. In: Hussain, C.M., Mishra, A.K. (Eds.), *New Polymer Nanocomposites for Environmental Remediation*. Elsevier, pp. 437–456.
- Jouault, N., Jestin, J., 2016. Intra-and interchain correlations in polymer nanocomposites: A small-angle neutron scattering extrapolation method. *ACS Macro Letters* 5, 1095–1099.
- Kausar, A., 2018. Review on polymer/halloysite nanotube nanocomposite. *Polymer-Plastics Technology and Engineering* 57, 548–564.
- Kazakova, M.A., Selyutin, A.G., Semikolenova, N.V., *et al.*, 2018. Structure of the in situ produced polyethylene based composites modified with multi-walled carbon nanotubes: In situ synchrotron x-ray diffraction and differential scanning calorimetry study. *Composites Science and Technology* 167, 148–154.
- Khalina, M., Sanei, M., Mobarakeh, H.S., Mahdavian, A.R., 2015. Preparation of acrylic/silica nanocomposites latexes with potential application in pressure sensitive adhesive. *International Journal of Adhesion and Adhesives* 58, 21–27.
- Khan, A.N., Ara, B., Gul, K., 2020. Electrochemical capacitance properties of electrode based on polyaniline coated graphite nanoplatelets/polystyrene composite film. *Journal of Electrochemical Energy Conversion and Storage* 17 (1).
- Khan, W.S., Hamadneh, N.N., Khan, W.A., 2016. Polymer nanocomposites—synthesis techniques, classification and properties. *Science and applications of Tailored Nanostructures* 50.
- Kim, D.J., Jo, M.J., Nam, S.Y., 2015. A review of polymer–nanocomposite electrolyte membranes for fuel cell application. *Journal of Industrial and Engineering Chemistry* 21, 36–52.
- Klevenz, H., 2004. Nanobiotechnology: From molecules to systems. *Engineering in Life Sciences* 4, 211–218.
- Kong, Q., Wu, T., Zhang, H., *et al.*, 2017. Improving flame retardancy of ifr/pp composites through the synergistic effect of organic montmorillonite intercalation cobalt hydroxides modified by acidified chitosan. *Applied Clay Science* 146, 230–237.
- Koo, J.H., 2006. *Polymer Nanocomposites*. McGraw-Hill Professional Pub.
- Krishnaiah, P., Ratnam, C.T., Manickam, S., 2017. Development of silane grafted halloysite nanotube reinforced polylactide nanocomposites for the enhancement of mechanical, thermal and dynamic-mechanical properties. *Applied Clay Science* 135, 583–595.
- Krump, H., Luyt, A., Hudec, I., 2006. Effect of different modified clays on the thermal and physical properties of polypropylene-montmorillonite nanocomposites. *Materials Letters* 60, 2877–2880.
- Kumar, A., Sharma, K., Dixit, A.R., 2019. A review of the mechanical and thermal properties of graphene and its hybrid polymer nanocomposites for structural applications. *Journal of materials science* 54, 5992–6026.
- Kumar, A., Negi, Y.S., Choudhary, V., Bhardwaj, N.K., 2014. Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste. *Journal of Materials Physics and Chemistry* 2, 1–8.
- Kumar, S., Sarita, Nehra, M., *et al.*, 2018. Recent advances and remaining challenges for polymeric nanocomposites in healthcare applications. *Progress in Polymer Science* 80, 1–38.
- Kumar, V., Lee, G., Singh, K., Choi, J., Lee, D.-J., 2020. Structure-property relationship in silicone rubber nanocomposites reinforced with carbon nanomaterials for sensors and actuators. *Sensors and Actuators A Physical* 303, 111712.
- Lampman, S., 2003. *Characterization and Failure Analysis of Plastics*. Asm International.
- Lasrado, D., Ahankari, S., Kar, K.J., 2020. Nanocellulose-based polymer composites for energy applications – A review. *Applied Polymer Science* 137, 48959.
- Lau, K.Y., M. Piah, M.A., 2011. Polymer nanocomposites in high voltage electrical insulation perspective: A review. *Malaysian Polymer Journal* 6.
- Lau, W.-J., Emadzadeh, D., Shahrin, S., Goh, P.S., Ismail, A.F., 2018. Chapter 9 – Ultrafiltration membranes incorporated with carbon-based nanomaterials for antifouling improvement and heavy metal removal. In: Ismail, A.F., Goh, P.S. (Eds.), *Carbon-Based Polymer Nanocomposites for Environmental and Energy Applications*. Elsevier, pp. 217–232.
- Lee, D., Sang, J.S., Yoo, P.J., *et al.*, 2019. Machine-washable smart textiles with photothermal and antibacterial activities from nanocomposite fibers of conjugated polymer nanoparticles and polyacrylonitrile. *Polymers* 11, 16.
- Lee, J.-H., Veyssset, D., Singer, J.P., *et al.*, 2012. High strain rate deformation of layered nanocomposites. *Nature Communications* 3, 1–9.
- Lemire, J.A., Harrison, J.J., Turner, R.J., 2013. Antimicrobial activity of metals: Mechanisms, molecular targets and applications. *Nature Reviews Microbiology* 11, 371–384.
- Leszczyńska, A., Njuguna, J., Pielichowski, K., Banerjee, J., 2007. Polymer/montmorillonite nanocomposites with improved thermal properties: Part I. Factors influencing thermal stability and mechanisms of thermal stability improvement. *Thermochimica acta* 453, 75–96.
- Li, F., Zhou, S., You, B., Wu, L., 2006. Kinetic investigations on the uv-induced photopolymerization of nanocomposites by ftir spectroscopy. *Journal of Applied Polymer Science* 99, 1429–1436.
- Li, X., Guo, Q., Yang, F., *et al.*, 2020. Electrical properties of Ildpe/Ildpe-g-ps blends with carboxylic acid functional groups for cable insulation applications. *ACS Applied Polymer Materials* 2, 3450–3457.
- Li, Y.-Q., Fu, S.-Y., Mai, Y.-W., 2006. Preparation and characterization of transparent zno/epoxy nanocomposites with high-uv shielding efficiency. *Polymer* 47, 2127–2132.
- Liao, J., Wei, X., Ran, B., *et al.*, 2017. Polymer hybrid magnetic nanocapsules encapsulating ir820 and PTX for external magnetic field-guided tumor targeting and multifunctional theranostics. *Nanoscale* 9, 2479–2491.
- Ling, J., Zhai, W., Feng, W., *et al.*, 2013. Facile preparation of lightweight microcellular polyetherimide/graphene composite foams for electromagnetic interference shielding. *ACS Applied Materials & Interfaces* 5, 2677–2684.
- Lionetto, F., Maffezzoli, A., 2008. Polymer characterization by ultrasonic wave propagation. *Advances in Polymer Technology: Journal of the Polymer Processing Institute* 27, 63–73.
- Lionetto, F., Maffezzoli, A., 2009. Rheological characterization of concentrated nanoclay dispersions in an organic solvent. *Applied Rheology* 19, 23423.
- Liu, J., Boo, W.-J., Clearfield, A., Sue, H.-J., 2006. Intercalation and exfoliation: A review on morphology of polymer nanocomposites reinforced by inorganic layer structures. *Materials and Manufacturing Processes* 21, 143–151.
- Liu, M., Jia, Z., Jia, D., Zhou, C., 2014. Recent advance in research on halloysite nanotubes-polymer nanocomposite. *Progress in Polymer Science* 39, 1498–1525.

- Liu, T., Phang, I.Y., Shen, L., Chow, S.Y., Zhang, W.-D., 2004. Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. *Macromolecules* 37, 7214–7222.
- Liu, X., Lu, X., Su, Y., Kun, E., Zhang, F., 2020. Clay-polymer nanocomposites prepared by reactive melt extrusion for sustained drug release. *Pharmaceutics* 12 (1), 51.
- Liu, Z., Chen, K., Yan, D., 2003. Crystallization, morphology, and dynamic mechanical properties of poly (trimethylene terephthalate)/clay nanocomposites. *European Polymer Journal* 39, 2359–2366.
- Loganathan, S., Valapa, R.B., Mishra, R.K., Pugazhenti, G., Thomas, S., 2017. Thermogravimetric analysis for characterization of nanomaterials. In *Thermal and Rheological Measurement Techniques for Nanomaterials Characterization*. Elsevier, pp. 67–108.
- Luo, J., Cheng, Z., Li, C., *et al.*, 2016. Electrically conductive adhesives based on thermoplastic polyurethane filled with silver flakes and carbon nanotubes. *Composites Science and Technology* 129, 191–197.
- Luo, Z., Gong, Y., Liao, X., Pan, Y., Zhang, H., 2016. Nanocomposite membranes modified by graphene-based materials for anion exchange membrane fuel cells. *RSC Advances* 6, 13618–13625.
- Mansor, M.R., Akop, M.Z., 2020. 9 - polymer nanocomposites smart materials for energy applications. In: Bouhfid, R., Qaiss, A. e.K., Jawaid, M. (Eds.), *Polymer Nanocomposite-Based Smart Materials*. Woodhead Publishing, pp. 157–176.
- Mariey, L., Signolle, J., Amiel, C., Travert, J., 2001. Discrimination, classification, identification of microorganisms using ftir spectroscopy and chemometrics. *Vibrational spectroscopy* 26, 151–159.
- Marinello, F., La Stora, A., Mauriello, G., Passeri, D., 2019. Atomic force microscopy techniques to investigate activated food packaging materials. *Trends in Food Science & Technology* 87, 84–93.
- Masoud, E.M., Liu, L., Peng, B., 2020. Synthesis, characterization, and applications of polymer nanocomposites. *Journal of Nanomaterials*. 2020.
- Mehta, V., Cooper, J.S., 2003. Review and analysis of pem fuel cell design and manufacturing. *Journal of Power Sources* 114, 32–53.
- Mishra, A.K., Valodkar, M.C., 2017. Polymer nanocomposites for energy and fuel cell applications. In: Tripathy, D.K., Sahoo, B.P. (Eds.), *Properties and Applications of Polymer Nanocomposites: Clay and Carbon Based Polymer Nanocomposites*. Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 107–137.
- Mittal, V., 2015. *Synthesis Techniques for Polymer Nanocomposites*. John Wiley & Sons.
- Morgan, A.B., Gilman, J.W., 2003. Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and x-ray diffraction: A comparative study. *Journal of Applied Polymer Science* 87, 1329–1338.
- Morgan, A.B., Wilkie, C.A., 2007. *Flame Retardant Polymer Nanocomposites*. John Wiley & Sons.
- Motoc, S., Remes, A., Pop, A., Manea, F., Schoonman, J., 2013. Electrochemical detection and degradation of ibuprofen from water on multi-walled carbon nanotubes-epoxy composite electrode. *Journal of Environmental Sciences* 25, 838–847.
- Müller, K., Bugnicourt, E., Latorre, M., *et al.*, 2017. Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields. *Nanomaterials* 7, 74.
- Munk, P., Aminabhavi, T.M., 1989. *Introduction to Macromolecular Science*. New York: Wiley.
- Munoz, S., Greenbaum, S., 2018. Review of recent nuclear magnetic resonance studies of ion transport in polymer electrolytes. *Membranes* 8, 120.
- Muñoz, J., Céspedes, F., Baeza, M., 2015. Modified multiwalled carbon nanotube/epoxy amperometric nanocomposite sensors with cuo nanoparticles for electrocatalytic detection of free chlorine. *Microchemical Journal* 122, 189–196.
- Mutiso, R.M., Winey, K.I., 2015. Electrical properties of polymer nanocomposites containing rod-like nanofillers. *Progress in Polymer Science* 40, 63–84.
- Nasouri, K., Shoushtari, A.M., Mirzaei, J., Merati, A.A., 2020. Synthesis of carbon nanotubes composite nanofibers for ultrahigh performance uv protection and microwave absorption applications. *Diamond and Related Materials* 107, 107896.
- Oberdisse, J., Banc, A., Genix, A.-C., 2017. Chain Structure of Polymer Nanocomposites Using Small-Angle Neutron Scattering. In: DEUNET Workshop, United Kingdom: Oxford.
- Oksman, K., Moon, R.J., 2014. Characterization of nanocomposites structure. In: Oksman, K., Mathew, A.P., Bismarck, A., Rojas, O.J. (Eds.), *Handbook of Green Materials: Bionanocomposites: Processing, Characterization and Properties*. World Scientific, pp. 89–105.
- Olya, N., Ghasemi, E., Ramezanzadeh, B., Mahdavian, M., 2020. Synthesis, characterization and protective functioning of surface decorated zn-al layered double hydroxide with SiO₂ nano-particles. *Surface and Coatings Technology* 387, 125512.
- Otaegi, I., Aranburu, N., Iturrondobeitia, M., Ibarretxe, J., Guerrica-Echevarría, G., 2019. The effect of the preparation method and the dispersion and aspect ratio of cnts on the mechanical and electrical properties of bio-based polyamide-4, 10/cnt nanocomposites. *Polymers* 11, 2059.
- Papon, A., Montes, H., Hanafi, M., *et al.*, 2012. Glass-transition temperature gradient in nanocomposites: Evidence from nuclear magnetic resonance and differential scanning calorimetry. *Physical Review Letters* 108, 065702.
- Paramane, A., Chen, X., Dai, C., *et al.*, 2020. Electrical insulation performance of cross-linked polyethylene/mgo nanocomposite material for ± 320 kv high-voltage direct-current cables. In: Jana, S.C. (Ed.), *Polymer Composites* 41. Wiley, pp. 1936–1949.
- Parameswaranpillai, J., Hameed, N., Kurian, T., Yu, Y., 2016. *Nanocomposite Materials: Synthesis, Properties and Applications*. CRC Press.
- Pavlović, V.B., Pavlović, V.P., 2021. Polymer-ceramic nanocomposites and converging technologies. In *Reference module in Materials Science and Materials Engineering*. Elsevier.
- Peng, H., Liu, X., Wang, G., *et al.*, 2015. Polymeric multifunctional nanomaterials for theranostics. *Journal of Materials Chemistry B* 3, 6856–6870.
- Peters, E.N., 2014. Chapter 9 – Thermoplastics, thermosets, and elastomers – Descriptions and properties. In *Mechanical Engineers' Handbook*. Wiley, pp. 1–48.
- Pina, S., Oliveira, J.M., Reis, R.L., 2015. Natural-based nanocomposites for bone tissue engineering and regenerative medicine: A review. *Advanced Materials* 27, 1143–1169.
- Pourhashem, S., Saba, F., Duan, J., *et al.*, 2020. Polymer/inorganic nanocomposite coatings with superior corrosion protection performance: A review. *Journal of Industrial and Engineering Chemistry* 88, 29–57.
- Rahman, M.R., Hamdan, S., Hui, J.L.C., 2017. Differential scanning calorimetry (dsc) and thermogravimetric analysis (tga) of wood polymer nanocomposites. In: *Proceedings of the MATEC web of conferences*, 03013. EDP Sciences.
- Rane, A.V., Kanny, K., Abitha, V., Thomas, S., 2018. Chapter 5 - Methods for synthesis of nanoparticles and fabrication of nanocomposites. In: Bhagyaraj, S.M., Oluwafemi, O. S., Kalarikkal, N., Thomas, S. (Eds.), *Synthesis of Inorganic Nanomaterials*. Elsevier, pp. 121–139.
- Rathod, V.T., Kumar, J.S., Jain, A., 2017. Polymer and ceramic nanocomposites for aerospace applications. *Applied Nanoscience* 7, 519–548.
- Rehman, S., Noman, M., Khan, A.D., *et al.*, 2020. Synthesis of polyvinyl acetate /graphene nanocomposite and its application as an electrolyte in dye sensitized solar cells. *Optik* 202, 163591.
- Reifarth, M., Hoepfner, S., Schubert, U.S., 2018. Uptake and intracellular fate of engineered nanoparticles in mammalian cells: Capabilities and limitations of transmission electron microscopy – Polymer-based nanoparticles. *Advanced Materials* 30, 1703704.
- Sahoo, T.R., 2017. Polymer nanocomposites for environmental applications. In: Tripathy, D.K., Sahoo, B.P. (Eds.), *Properties and Applications of Polymer Nanocomposites*. Springer, pp. 77–106.
- Sahoo, B.P., Tripathy, D.K., 2017. Chapter 1 – Introduction to Clay-and Carbon-Based Polymer Nanocomposites: Materials, Processing, and Characterization. In: Tripathy, D.K., Sahoo, B.P. (Eds.), *Properties and Applications of Polymer Nanocomposites*. Springer, 1–24.
- Sakurai, S., 2017. Recent developments in polymer applications of synchrotron small-angle x-ray scattering. *Polymer International* 66, 237–249.
- Saleh, T.A., Shetti, N.P., Shanbhag, M.M., Raghava Reddy, K., Aminabhavi, T.M., 2020. Recent trends in functionalized nanoparticles loaded polymeric composites: An energy application. *Materials Science for Energy Technologies* 3, 515–525.

- Salehoun, E., Ahmadi, S.J., Razavi, S.M., Parvin, N., 2017. Thermal and corrosion resistance properties of unsaturated polyester/clay nanocomposites and the effect of electron beam irradiation. *Polymer Bulletin* 74, 1629–1647.
- Sandler, J., Windle, A., Werner, P., *et al.*, 2003. Carbon-nanofibre-reinforced poly (ether ether ketone) fibres. *Journal of Materials Science* 38, 2135–2141.
- Sarwar, S., Chen, W., Waheed, R., 2017. Electricity consumption, oil price and economic growth: Global perspective. *Renewable and Sustainable Energy Reviews* 76, 9–18.
- Schmidt, R., Fitzek, H., Nachtnebel, M., *et al.*, 2019. The combination of electron microscopy, raman microscopy and energy dispersive x-ray spectroscopy for the investigation of polymeric materials. In *Macromolecular Symposia*. Wiley Online Library. 1800237.
- Shah, K.J., Shukla, A.D., Shah, D.O., Imae, T., 2016. Effect of organic modifiers on dispersion of organoclay in polymer nanocomposites to improve mechanical properties. *Polymer* 97, 525–532.
- Shen, R., Hatanaka, L.C., Ahmed, L., *et al.*, 2017. Cone calorimeter analysis of flame retardant poly (methyl methacrylate)-silica nanocomposites. *Journal of Thermal Analysis and Calorimetry* 128, 1443–1451.
- Shibayama, M., Karino, T., Miyazaki, S., *et al.*, 2005. Small-angle neutron scattering study on uniaxially stretched poly (n-isopropylacrylamide) — clay nanocomposite gels. *Macromolecules* 38, 10772–10781.
- Singh, R., Kulkarni, S.G., 2014. Nanocomposites based on transition metal oxides in polyvinyl alcohol for emi shielding application. *Polymer Bulletin* 71, 497–513.
- Solomon, M.M., Gerengi, H., Umoren, S.A., 2017. Carboxymethyl cellulose/silver nanoparticles composite: Synthesis, characterization and application as a benign corrosion inhibitor for st37 steel in 15% h2so4 medium. *ACS Applied Materials & Interfaces* 9, 6376–6389.
- Son, D., Cho, S., Nam, J., Lee, H., Kim, M., 2020. X-ray-based spectroscopic techniques for characterization of polymer nanocomposite materials at a molecular level. *Polymers* 12, 1053.
- Stewart, R., 2009. Lightweighting the automotive market. *Reinforced Plastics* 53, 14–21.
- Suhail, M.H., Abdullah, O.G., Kadhim, G.A., 2019. Hydrogen sulfide sensors based on pani/f-swcnt polymer nanocomposite thin films prepared by electrochemical polymerization. *Journal of Science: Advanced Materials and Devices* 4, 143–149.
- Sun, R., Li, L., Feng, C., Kitipornchai, S., Yang, J., 2018. Tensile behavior of polymer nanocomposite reinforced with graphene containing defects. *European Polymer Journal* 98, 475–482.
- Sunday, A., Balogun, S., Akpan, E., 2012. Review of green polymer nanocomposites. *Journal of Minerals and Materials Characterization and Engineering* 11.
- Suzuki, S., Kawai, K., Ashoori, F., *et al.*, 2000. Long-term follow-up study of artificial dermis composed of outer silicone layer and inner collagen sponge. *British Journal of Plastic Surgery* 53, 659–666.
- Taha, T., 2017. Optical and thermogravimetric analysis of pb 3 o 4/pvc nanocomposites. *Journal of Materials Science: Materials in Electronics* 28, 12108–12114.
- Thompson, C.M., Herring, H.M., Gates, T.S., Connell, J.W., 2003. Preparation and characterization of metal oxide/polyimide nanocomposites. *Composites Science and Technology* 63, 1591–1598.
- Tschöpe, A., Birringer, R., 2001. Grain size dependence of electrical conductivity in polycrystalline cerium oxide. *Journal of electroceramics* 7, 169–177.
- Umoren, S.A., Madhankumar, A., 2016. Effect of addition of Ceo2 nanoparticles to pectin as inhibitor of X60 steel corrosion in HCL medium. *Journal of Molecular Liquids* 224, 72–82.
- Umoren, S.A., Solomon, M.M., 2019. Protective polymeric films for industrial substrates: A critical review on past and recent applications with conducting polymers and polymer composites/nanocomposites. *Progress in Materials Science* 104, 380–450.
- Vatanpour, V., Safarpour, M., 2018. Chapter 12 – Carbon-based polymer nanocomposite membranes for desalination. In: Ismail, A.F., Goh, P.S. (Eds.), *Carbon-Based Polymer Nanocomposites for Environmental and Energy Applications*. Elsevier, pp. 281–304.
- Wan, T., Chen, D., 2018. Mechanical enhancement of self-healing waterborne polyurethane by graphene oxide. *Progress in Organic Coatings* 121, 73–79.
- Wang, Q., Zhu, L., 2011. Polymer nanocomposites for electrical energy storage. *Journal of Polymer Science* 49, 1421–1429.
- Wang, X., Wu, L., Li, J., 2011. Synergistic flame retarded poly(methyl methacrylate) by nano-ZrO₂ and triphenylphosphate. *Journal of Thermal Analysis and Calorimetry* 103, 741–746.
- Wang, Y., Su, J., Li, T., *et al.*, 2017. A novel uv-shielding and transparent polymer film: When bioinspired dopamine-melanin hollow nanoparticles join polymers. *ACS Applied Materials & Interfaces* 9, 36281–36289.
- Xu, S., Li, S.-Y., Zhang, M., *et al.*, 2020. Fabrication of green alginate-based and layered double hydroxides flame retardant for enhancing the fire retardancy properties of polypropylene. *Carbohydrate Polymers* 234, 115891.
- Yadav, C., Saini, A., Maji, P.K., 2017. Energy efficient facile extraction process of cellulose nanofibres and their dimensional characterization using light scattering techniques. *Carbohydrate polymers* 165, 276–284.
- Yang, C., Wei, H., Guan, L., *et al.*, 2015. Polymer nanocomposites for energy storage, energy saving, and anticorrosion. *Journal of Materials Chemistry A* 3, 14929–14941.
- Yei, D.-R., Kuo, S.-W., Su, Y.-C., Chang, F.-C., 2004. Enhanced thermal properties of ps nanocomposites formed from inorganic poss-treated montmorillonite. *Polymer* 45, 2633–2640.
- Yu, S., Lee, S.H., Han, J.A., *et al.*, 2020. Insulative ethylene-propylene copolymer-nanostructured polypropylene for high-voltage cable insulation applications. *Polymer* 202, 122674.
- Zafar, R., Zia, K.M., Tabasum, S., *et al.*, 2016. Polysaccharide based bionanocomposites, properties and applications: A review. *International Journal of Biological Macromolecules* 92, 1012–1024.
- Zanetti, M., Kashiwagi, T., Falqui, L., Camino, G., 2002. Cone calorimeter combustion and gasification studies of polymer layered silicate nanocomposites. *Chemistry of Materials* 14, 881–887.
- Zare, Y., Shabani, I., 2016. Polymer/metal nanocomposites for biomedical applications. *Materials Science and Engineering: C* 60, 195–203.
- Zhang, X., Yang, P., Dai, Y., *et al.*, 2013. Multifunctional up-converting nanocomposites with smart polymer brushes gated mesopores for cell imaging and thermo/pHdual-responsive drug controlled release. *Advanced Functional Materials* 23, 4067–4078.
- Zhang, Y., Zhuang, S., Xu, X., Hu, J., 2013. Transparent and UV-shielding ZnO@PMMA nanocomposite films. *Optical Materials* 36, 169–172.
- Zhen, W., Zheng, Y., 2016. Synthesis, characterization, and thermal stability of poly (lactic acid)/zinc oxide pillared organic saponite nanocomposites via ring-opening polymerization of d, l-lactide. *Polymers for Advanced Technologies* 27, 606–614.
- Zhu, Y., Cao, K., Chen, M., Wu, L., 2019. Synthesis of uv-responsive self-healing microcapsules and their potential application in aerospace coatings. *ACS Applied Materials & Interfaces* 11, 33314–33322.

Effect of Fiber Orientation on the Mechanical Properties of Laminated Polymer Composites

N Ghamarian and Mohamed AA Hanim, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

P Penjumras, Universiti Putra Malaysia, Serdang, Selangor, Malaysia and Maejo University-Phrae Campus, Phrae, Thailand

Dayang LA Majid, University Putra Malaysia, Serdang, Selangor Darul Ehsan, Malaysia

© 2016 Elsevier Inc. All rights reserved.

This is a reproduction of N Ghamarian, M.A. Azmah Hanim, P Penjumras, D.L. Majid, Effect of Fiber Orientation on the Mechanical Properties of Laminated Polymer Composites, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2016, doi:[10.1016/B978-0-12-803581-8.04083-2](https://doi.org/10.1016/B978-0-12-803581-8.04083-2).

Introduction

A composite material is a combination of two or more distinct materials into one with the intent of suppressing the undesirable properties of the constituent materials in favor of the desirable properties [1]. Fiber-reinforced plastic (FRP) composites are typically fabricated using a polymer matrix, such as epoxy, vinyl ester, or polyester and reinforced with various grades of carbon, glass, and/or fibers [1].

Polymers are playing an important role in the contemporary world for a number of applications ranging from daily needs to the biomedical and defense fields [2]. Recently the field of polymer science has attracted greater attraction from the research community due to the enormous advantages offered by polymer based materials, and several polymers are appearing from the laboratories of scientists with unique and important properties for advanced applications [2]. Polymer based composite materials have been playing an important role in niche applications in the last few decades, ever since the discovery of Bakelite resin [2]. These materials are emerging rapidly as a potential substitute for metal or ceramic based materials in a number of fields including automotive, aerospace, marine, sporting goods, and electronic industries, etc. [2]. Among the various composite materials, natural FRP composites are coming under increasing scrutiny due to their easy processing and enormous eco-friendly advantages [2]. The potential advantages present in the use of FRP composites include: higher strength, lighter weight, higher performance, longer lasting, rehabilitating existing structures and extending their life, seismic upgrades, defense systems' unique requirements, space systems, and ocean environments [1].

Two commonly used glass fibers in the industry are E-glass and S-glass. The primary material in most glass fibers is silica; to effectively produce these fibers, the ingredients must be melted in a furnace at a temperature of about 1370 °C. Glass fibers are a popular choice for fiber reinforcement due to their advantageous properties such as high strength (tensile strength of approximately 3.40 GPa), tolerance to high temperatures and corrosive environments, and low cost [1].

FRP composites are extremely important in industry and have attracted tremendous attention [3]. Glass fiber (GF) has stimulated tremendous interest as a reinforcement for the polymer matrix due to its very low cost, high mechanical property, good heat and resistance [3]. For GF/polymer composites, the interface between the GF and the polymer plays an important role in controlling some of the mechanical properties. In order to obtain high-performance FRP composites, high interfacial strength is the key issue [3]. FRP composites are widely used in many engineering applications involving wide temperature changes such as in aircraft structural components and wind turbine blades, and for retrofitting nuclear reactor containment concrete structures, etc. [4, 5]. In previous research, a fiber angle of 45 degrees and 8 layers of glass fiber were investigated [6]. Among all the geometries, the 45 degree geometry was found to have the highest Filtration Index. The 45 degree geometry indicated a Filtration Index improvement of up to 4.3 times that of the base case.

The objectives of this research are to study the mechanical properties through tensile testing of woven fabric glass epoxy composite laminates. The orientations of the glass composites are 90, 60, and 45°.

Theory

Definition of Composites

A composite material is made by combining two or more materials to give a unique combination of properties. It can include metal alloys, plastic co-polymers, minerals, and wood. Fiber-reinforced composite materials differ from these materials in that the constituent materials are different at the molecular level and are mechanically separable. In bulk form, the constituent materials work together but remain in their original forms. The final properties of composite materials are better than the constituent material properties [7].

The concept of composite materials was not invented by human beings; it is found in nature. An example is wood, which is a composite of cellulose fibers in a matrix of natural glue called lignin. Scientists have found that the fibers taken from a spider's web are stronger than synthetic fibers. The main concept of a composite is that it contains matrix materials. Typically, composite material is formed by reinforcing fibers in a matrix resin as shown in Fig. 1. The reinforcements can be fillers in particulates, or whiskers, and the matrix materials can be metals, plastics, or ceramics. The fibers can be continuous, long, or short. Composites made with a polymer matrix have become more common and are widely used in various industries. The reinforcing fiber or fabric

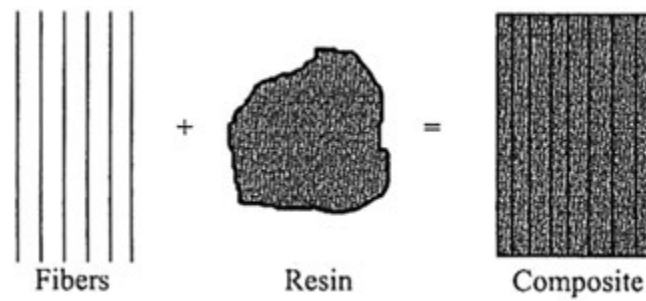


Fig. 1 Formation of a composite material using fibers and resin [7].

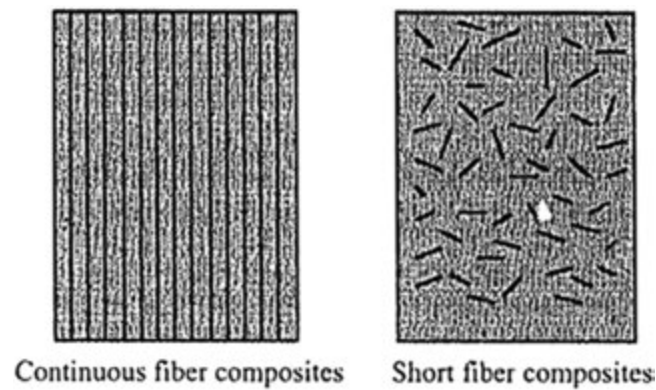


Fig. 2 Continuous fiber and short fiber composite [7].

provides strength and stiffness to the composite, whereas the matrix gives rigidity and environmental resistance. Reinforcing fibers are found in different forms, from long continuous fibers to woven fabric to short chopped fibers and mat. The properties strongly depend on the way the fibers are laid in the composite. The important thing about composites is that the fiber carries the load and its strength is greatest along the axis of the fiber. Long continuous fibers in the direction of load result in a composite with properties far exceeding the matrix resin itself. The same material chopped into short lengths yields lower properties than continuous fibers, as illustrated in Fig. 2.

Phases of Composites

A composite material is formed by reinforcing plastics with fibers. The important functions of fibers and matrix materials are discussed in the following sections [7].

The main functions of the fibers in a composite are:

1. To carry the load. In a structural composite, 70–90% of the load is carried by the fibers.
2. To provide stiffness, strength, thermal stability, and other structural properties in the composites.
3. To provide electrical conductivity or insulation, depending on the type of fiber used.

A matrix material fulfills several functions in a composite structure, most of which are vital to the satisfactory performance of the structure. Fibers by themselves are of little use without the presence of a matrix material or binder.

The important functions of a matrix material include the following:

1. The matrix material binds the fiber together and transfers the load to the fibers. It provides rigidity and shape to the structure.
2. The matrix isolates the fibers so that individual fibers can act separately. This stops or slows the propagation of a crack.
3. The matrix provides a good surface finish quality and aids in the production of net-shape parts.
4. The matrix provides protection to reinforcing fibers against chemical attack and mechanical damage (wear).
5. Depending on the matrix material selected, performance characteristics such as ductility, impact strength, etc. are also influenced. A ductile matrix will increase the toughness of the structure. For higher toughness requirements, thermoplastic-based composites are selected.
6. The failure mode is strongly affected by the type of matrix material used in the composite as well as its compatibility with the fiber.

Table 1 Glass grades for fiberglass [8]

Type	Description
A	Glass of soda-lime composition similar to bottle glass. Poor thermal and chemical properties, not used for fibers.
C	Chemically resistant soda-lime-borosilicate glass used for its high corrosion and chemical attack resistance.
D	A low-density glass with high electrical resistance.
E	Pyrex composition glass. Good electrical properties and good for general-purpose application when a combination of good strength and chemical resistance is observed.
S	A high-strength, high-modulus glass for specific applications. Higher in cost.

2.2.1 Fiber

Fiber for composite materials can come in many forms: discontinuous fibers, long fibers, short fibers, organic fibers, inorganic fibers. The most widely used materials in FRPs are glass, carbon, aramid, and boron [7].

2.2.1.1 Fiberglass

Fiberglass is one of the most versatile and most widely used fibrous reinforcing materials. Due to its extensive usage, it is available in a wide variety of configurations, including continuous filaments with twisted or parallel strands, short chopped fibers, woven cloth, rovings, and preregs. Glass fibers are produced by passing molten glass through a platinum crucible (the bushing) which contains many small holes (tips) through which the glass is drawn, forming the fibrous material. Immediately on passing through the tips, the drawn glass fibers are subjected to a carefully controlled water spray and a humidity- and temperature-controlled air blast for rapid cooling. The glass is then coated with an appropriate size and then wound on mandrils for packaging and further handling. The sizing is usually a starch-oil emulsion which absorbs water to provide lubrication during the subsequent winding and handling operations.

Fibers are manufactured in the range of 10–25 μm . The thinner-diameter fibers can be more easily wetted and coated by resin and provide a better drape to contour accurately a complex mold. However, they are more difficult to produce and require more care in handling. **Table 1** lists the various glass grades available in fibers. Glass fibers are amorphous and behave elastically until their breaking point, failing with about 3% elastic strain. Over 90% of the fiberglass used for reinforcement is of the E-glass type. This glass has excellent electrical properties and good mechanical properties and bonds well to most plastics after an appropriate coupling agent is employed. S-glass is higher in strength but difficult to manufacture and is utilized primarily in aerospace applications where strength is critical. Chemically resistant C-glass is utilized when chemical resistance is a critical requirement. The C-glass is usually employed as an outer layer with the more customary E-glass as the bulk of the fiberglass structure [8].

Carbon fiber

Carbon and graphite fibers are produced using polyacrylonitrile (PAN) and pitch. Fibers of these starting materials are produced by the techniques for fiber manufacture, in which a solution of the polymer is forced through a spinneret head containing minute holes to produce fine fibers. These starting fibers are converted to carbon by decomposition at elevated temperature in a series of heating steps in air and inert atmospheres to temperatures as high as 3000 $^{\circ}\text{C}$. All components except the carbon evaporate at these temperatures, and the crystal structure changes simultaneously. The fibers are stretched to align the molecules along the fiber axis, either prior to or concurrent with the heating process. The graphite fibers are given various surface treatments, and coupling agents are applied to the surface to improve their compatibility with the resin matrix [8].

Aramid fiber

Aramid fiber (trade name Kevlar) is manufactured by Dupont [8]. Aramid fibers provide the highest tensile strength-to-weight ratio among reinforcing fibers. They provide good impact strength like carbon fibers; they provide a negative coefficient of thermal expansion. The disadvantage of aramid fibers is that they are difficult to cut and machine [7].

Boron fiber

The modulus of boron is the highest of the high-strength fibers, and boron is used in applications where maximum stiffness is required. The boron fibers are manufactured starting with boron trichloride (BCl_3), which is reduced with hydrogen to generate the boron. Due to its high cost and the difficulties associated with handling boron, this material is less commonly used than carbon or Kevlar fiber.

Matrix material

Matrix materials are compounded with reinforcing materials. Among the fibers, glass is the main reinforcement. Examples of these matrix materials are as follows:

Epoxy

The starting materials for the epoxy matrix are low molecular weight organic liquid resins containing a number of epoxide groups, which are simply three-membered rings with one oxygen and two carbon atoms (**Fig. 3**).

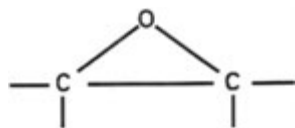


Fig. 3 Characteristic group for epoxies [9].

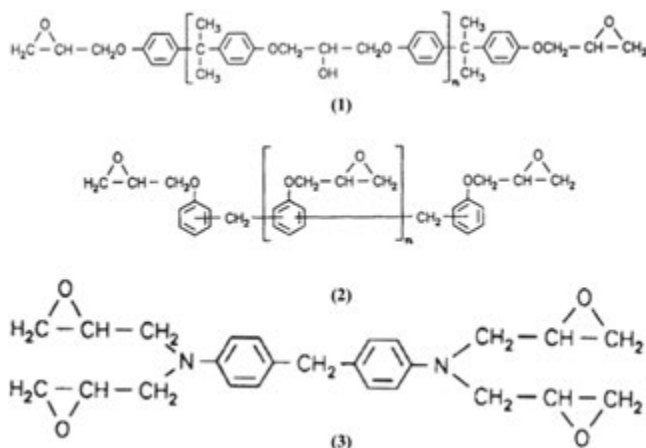


Fig. 4 Difunctional epoxy (1), epoxidised novolak (2), and tetraglycidyl methylene dianiline (3) [9].

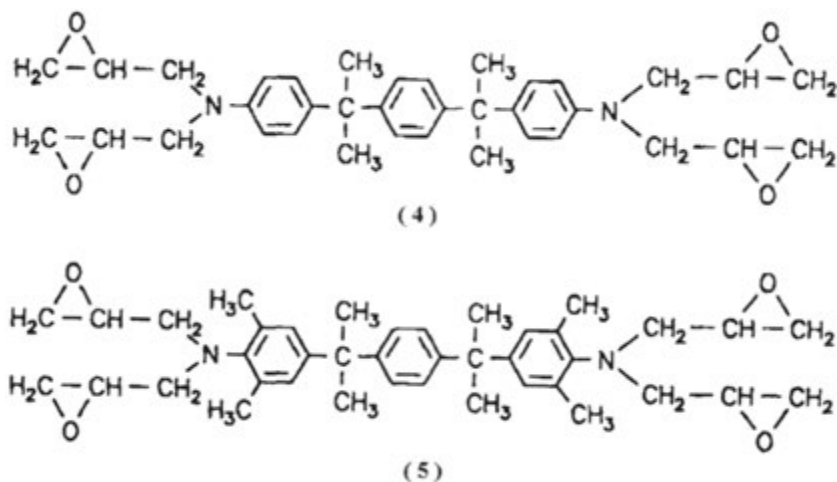


Fig. 5 New generation aromatic and glycidyl amine resins [9].

Epoxides can vary from difunctional to polyfunctional. After their reaction with the curing agents (which occurs without the evolution of any by-product), they yield to high performance systems with a combination of high rigidity, solvent resistance and elevated temperature behavior. The most widely used difunctional epoxy is the diglycidyl ether of bisphenol A, with (n) from 0.2 to 12 (formula 1 in Fig. 4) with the use of different types of curing agents, i.e., various amines. Epoxidised novolaks (formula 2) possess multi-epoxy functionality of at least 2, or more than 5, epoxy groups per molecule.

For high temperature aerospace applications, a special polyfunctional epoxy with aromatic and heterocyclic glycidyl amine groups, i.e., tetraglycidyl methylene dianiline (TGMDA; formula 3), is used.

A new generation of aromatic and glycidyl amine resins with improved hot/wet temperature characteristics is also available (formulae 4 and 5 in Fig. 5). There are, in addition, a number of special multi-functional epoxides formulated with TGMDA and/or bisphenol A.

Curing agents used for epoxides are either co-reactants (become incorporated with the epoxide during the reaction), or act as a catalyst to promote crosslinking. The first type of curing agent is polyfunctional and can be basic (primary/secondary amines, polyaminoamides) or acidic (anhydrides, polyphenols, polymeric thiols). Depending on the basicity or acidity of the curing agent,

curing may occur at room or at high temperatures. Catalytic curing agents (tertiary amines and BF_3 complexes) can accelerate curing at low or at ambient temperatures.

Selection of the epoxy resin for any composite application is usually done by considering the final application conditions of the composite, since there are significant differences existing between the thermal and mechanical properties of different epoxides, i.e., in moduli, in strain to failure and in T_g , and usually there is a compromise between the high temperatures and toughnesses. That is, the T_g controls the application temperature, which is high (247°C) for brittle epoxides, but much lower for toughened epoxides. The degree of polymerization can also affect processability and crosslink densities. In addition, the type of curing agent or accelerator and its molar ratio to the epoxy affects some of the final properties of the epoxy system, and these must be optimized, because of a change in crosslink densities. For structural applications, the hardener dicyandiamide (DICY) is usually used. By careful selection of the polymer and curing agent to accelerator ratio, and their use with the optimized values, the properties of the final product can be assured. In addition, there are a number of methods and strategies which have been developed for the combination of the most desirable features of a thermoplastic resin segment within the epoxy resin to form a multi-component composite system. A considerable amount of research has been done to further improve the toughness, moisture resistance and heat stability of epoxy matrices. These studies led to the production of epoxy composite systems for subsonic aircraft with the desired tensile-compressive moduli and tensile strength values of 138 GPa and 1930 MPa. In comparison, a tensile-compression modulus of 3100 MPa and a tensile strength value of 96 MPa was recorded for the neat resin.

Epoxy resins have the added advantage over many other thermosets in that, since no volatiles and condensation products other than the polymer product are produced during cure, molding does not require, in principle, high pressure molding equipment. By use of the epoxy matrix, one can gain a system with the following advantages [9]:

- 1) a wide variety of properties,
- 2) low shrinkage during cure (lowest within thermosets),
- 3) good resistance to most chemicals,
- 4) good adhesion to most fiber, fillers,
- 5) good resistance to creep and fatigue, and
- 6) good electrical properties.

Conversely, the following principal disadvantages may apply:

- 1) Sensitivity to moisture (after moisture absorption (1–6%), there is usually a decrease in the following: heat distortion point, dimensions and physical properties),
- 2) difficulty in combining toughness and high-temperature resistances (as explained above),
- 3) high CTE as compared to other thermosets,
- 4) susceptibility to UV degradation, and
- 5) cost (epoxies are more expensive than polyesters).

Phenolics

Phenolics (produced by reacting phenol with formaldehyde/PE) were the original major commercially viable synthetic thermoset (TS) plastic materials. They have low creep, excellent dimensional stability, good water and chemical resistance, heat resistance and good weatherability. Phenolic resins are inherently brittle, giving poor impact performance, but by adding materials such as siloxane and glass fibers this is significantly increased.

Compounds from these resins have been produced with glass, natural, and other fibers. Principally compression, transfer, and injection molding are used to process them. There are phenolics that when processed release water and others that do not release water. They offer an advantage compared with TS polyesters: i.e., a degree of good inherent resistance to heat and combination. Compared to most other materials they have lower mechanical properties [10].

Polyesters (TS)

Polyesters are low-cost resin systems and offer excellent corrosion resistance. Polyester can be a thermosetting resin and a thermoplastic resin [8]. Polyesters can be used on their own in applications such as casting and encapsulation/potting and in pastes and concretes. Their largest field of application, however, is in reinforced polymers (RPs), where glass fiber in different forms is the main type of reinforcement, offering a cost/performance profile that complements that of the resin. There are many variations of resin on the market, adapted to different applications [10].

Fabrics

There are two major types of fabrics available in the composites industry: woven fabrics and nonwoven (noncrimp) fabrics [7].

Woven fabrics

Woven fabrics are used in trailers, containers, barge covers and water tower blades, and in other marine wet lay-up applications. These fabrics are woven yarns, rovings, or tows in mat in a single layer. Common weave styles are shown in Fig. 6. The amount of fiber in different directions is controlled by the weave pattern. For example, in unidirectional woven fabrics, fibers are woven in

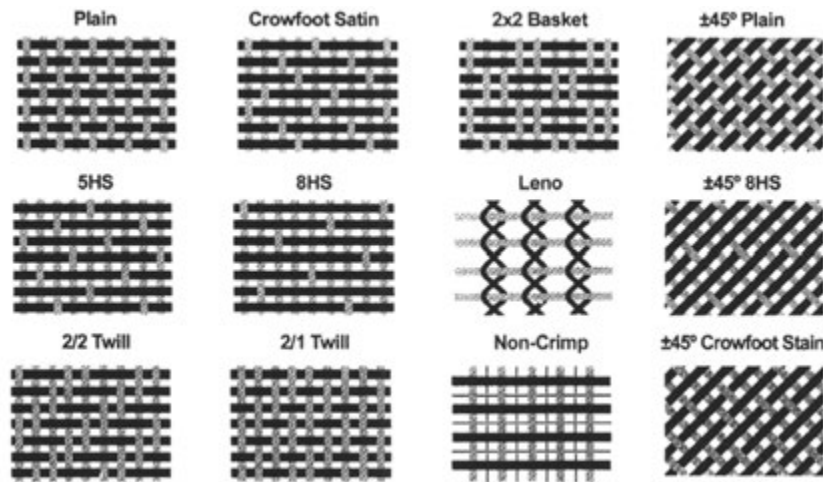


Fig. 6 Various weave styles for fabrics [7].

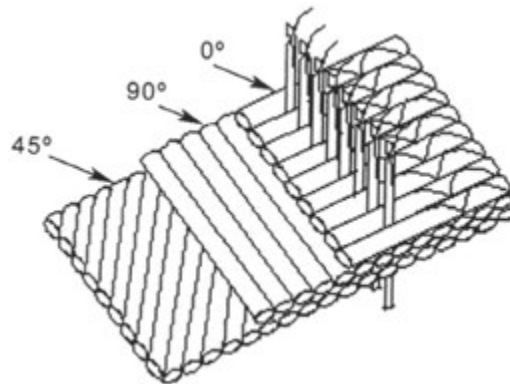


Fig. 7 Schematic of noncrimp fabrics [7].

such a way that the fibers in 0° are up to 95% of the total weight of the fabric. In a plain-weave pattern, fibers in 0° and 90° directions are equally distributed.

Noncrimp fabrics

In noncrimp fabrics, yarns are placed parallel to each other as shown in Fig. 7 and then stitched together using polyester thread. Warp unidirectional fabric is used when fibers are needed in one direction only. In fabrics, reinforcements are laid 0° (or warp direction) only as shown in Fig. 8; whereas in weft unidirectional fabrics, reinforcements are laid at 90° (or weft direction) only as shown in Fig. 9. Weft fabrics are typically used in filament wound tubes and pipes and also pultruded components where reinforcement in the weft direction is necessary [7].

Mechanical Properties

Stress-strain diagram

In order to relate the loads on engineering structures to the deformation produced by the loads, experiments must be performed to determine the load-deformation behavior of the materials used in fabricating the structures. Many useful mechanical properties are obtained from tension tests or compression tests [11]. A basic understanding of the stress-strain behavior of materials is of utmost importance to design engineers. One such typical stress-strain (load-deformation) diagram is illustrated in Fig. 10 [12].

Stress: the force applied to produce deformation in a unit area of a test specimen. Stress is a ratio of applied load to the original cross-sectional area.

Strain: the ratio of the elongation to the gage length of the test specimens, or simply stated, the change in length per unit of the original length ($\Delta l/l$). It is expressed as a dimensionless ratio.

Elongation: the increase in length of the test specimen produced by a tensile load.

Yield point: the first on the stress-strain curve at which an increase in strain occurs without an increase in stress.

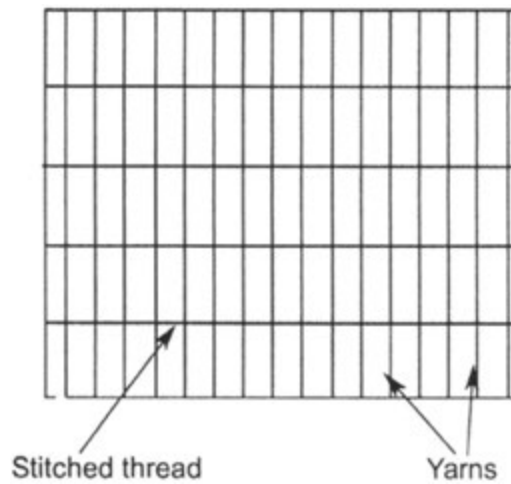


Fig. 8 Warp unidirectional fabrics [7].

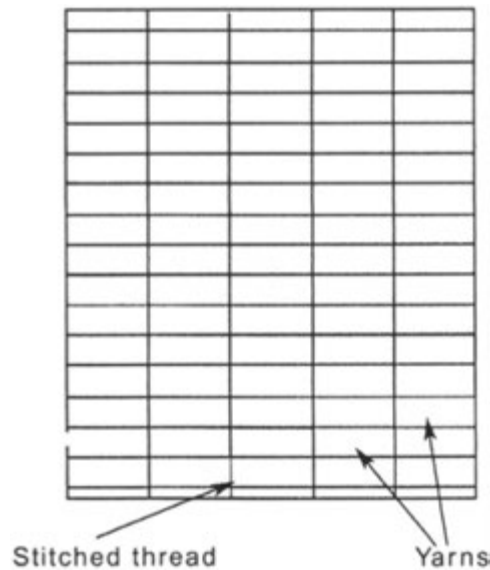


Fig. 9 Weft unidirectional fabrics [7].

Yield strength: the stress at which a material exhibits a specified limiting deviation from the proportionality of stress to strain. Unless otherwise specified, this stress will be at the yield point.

Proportional limit: the greatest stress at which a material is capable of sustaining the applied load without any deviation from the proportionality of stress to strain (Hooke's Law).

Modulus of elasticity: the ratio of stress to the corresponding strain below the proportional limit of the material. It is expressed in F/A . This is also known as Young's modulus. A modulus is a measure of the material's stiffness.

Ultimate strength: the maximum unit stress a material will withstand when subjected to an applied load in compression, tension, or shear.

Secant modulus: the ratio of the total stress to the corresponding strain at any specific point on the stress-strain curve.

The stress-strain diagram illustrated in **Fig. 10** is typical of that obtained in tension for a constant rate of loading. However, the curves obtained from other loading conditions, such as compression or shear, are quite similar in appearance.

The initial portion of the stress-strain curve between point A and C is linear and it follows Hooke's law, which states that for an elastic material the stress is proportional to the strain. The point C at which the actual curve deviates from the straight line is called the proportional limit, meaning that only up to this point is stress proportional to strain. The behavior of material below the proportional limit is elastic in nature and therefore the deformations are recoverable.

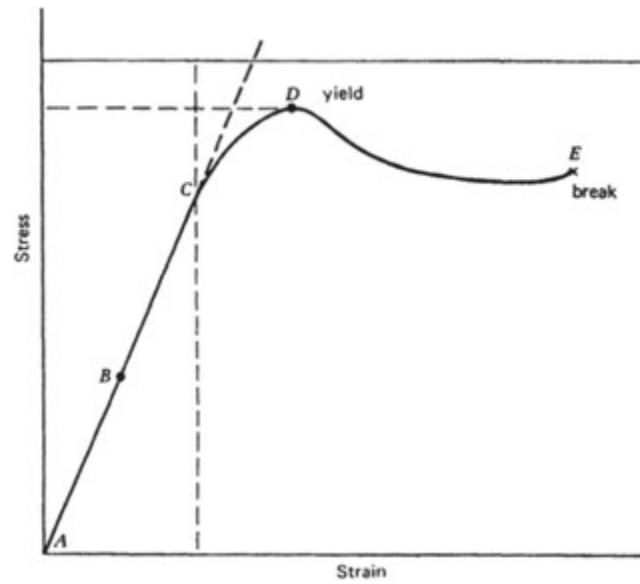


Fig. 10 A typical stress-strain curve [12].

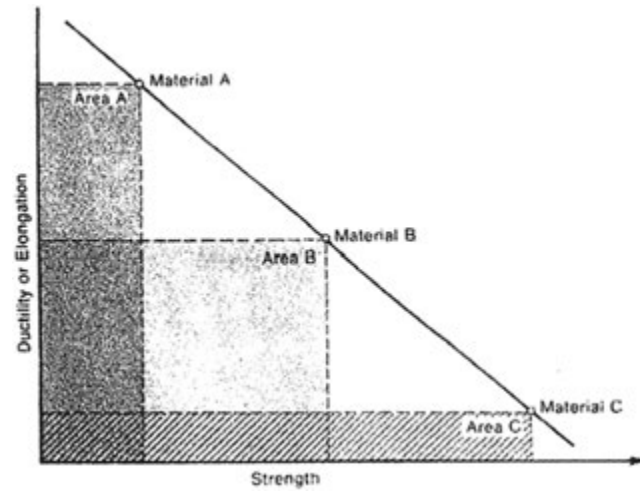


Fig. 11 Relation between ductility and strength [12].

The area under the stress-strain curve is considered to be the toughness of the polymeric material. Fig. 11 illustrates the relation between ductility and strength.

The matrix material transmits the force to the fibers, which carry most of the applied force. The matrix also provides protection for the fiber surface and minimizes the diffusion of species such as oxygen or moisture that can degrade the mechanical properties of the fibers. The mechanical properties of FRPs are related to the mechanical properties and fractional volume of each phase, matrix and reinforcement. This is called the rule of mixture. By using the rule of mixture, the properties as well as the strength, the modulus of elasticity, the density, and the electrical and thermal conductivity are predictable. In addition, the rule of mixture is used to predict the modulus of elasticity when the fibers are continuous and unidirectional [13]. Parallel to the fibers, the modulus of elasticity may be as high as:

$$E_c = f_m E_m + f_f E_f \quad [1]$$

where f is the volume fraction and the subscripts m and f refer to the matrix and the fiber. Note that $f_m = 1 - f_f$.

However, when the applied stress is very large, the matrix begins to deform and the stress-strain curve is no longer linear as in Fig. 12. Since the matrix now contributes little to the stiffness of the composite, the modulus can be approximated by:

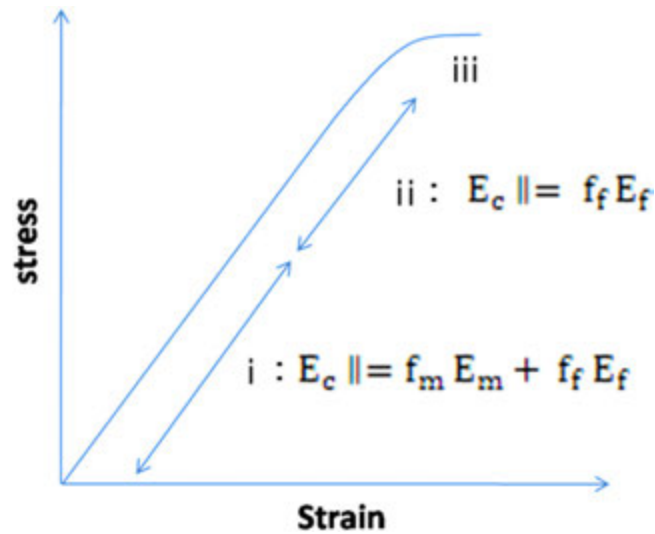


Fig. 12 The stress-strain curve for a fiber-reinforced composite [13].

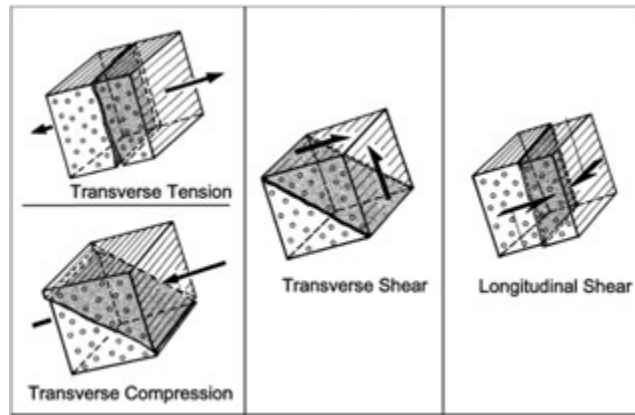


Fig. 13 Different forms of IFF [14].

$$E_c = f_f E_f \quad [2]$$

Fig. 12 demonstrates that at low stresses (region i), the modulus of elasticity is given by the rule of mixtures. At higher stresses (region iii), the matrix deforms and the rule of mixture is no longer obeyed [13].

Attention must be paid to the fact that different combinations of stresses lead to different forms of Inter Fiber Fracture (IFF). This is of major importance since some forms of IFF are harmless for certain applications whereas other forms lead inevitably to structural failure [14] (**Fig. 13**).

Design properties

From the design standpoint, the most significant stress-strain properties can be categorized under three headings [11].

Strength

There are three strength values of interest:

- (1) The yield strength is the highest stress that the material can withstand without undergoing significant yielding.
- (2) The ultimate strength is the maximum value of stress that the material can withstand.
- (3) The fracture stress, if different from the ultimate stress, may be of interest. It is the value of the stress at fracture.

Stiffness

The stiffness of a material is basically the ratio of stress to strain. Stiffness is of interest primarily in the linearly elastic region; therefore, Young's modulus is the value used to represent the stiffness of a material.

Ductility

Materials that can undergo large strain before fracture are classified as ductile materials; those that fail at small values of strain are classified as brittle materials. Strictly speaking, the terms ductile and brittle refer to the mode of fracture, and a material like structural steel, which behaves in a ductile manner at room temperature, may exhibit brittle behavior at very low temperatures. Therefore, when we speak of a 'brittle material' or a 'ductile material', we are referring to the room temperature behavior of the material.

The two commonly used measures of ductility are the percentage of elongation and the percentage of reduction in the area at the section where fracture occurs (the area reduction is expressed as a percentage of the original area).

Factors affecting mechanical properties

Many factors must be considered when designing an FRP composite, including the length, diameter, orientation, amount and properties of the fibers, the matrix and the bonding between the fibers and the matrix.

Specimen size and specimen preparation

In the case of fiber length and diameter, it should be considered that fibers can be short, long, or even continuous. Their dimensions are often characterized by the aspect ratio of d/l where l is the fiber length and d is the diameter. Typical fibers have a diameter varying from 10 to 150 μm . The strength of the composite improves when the aspect ratio is large. Generally, the aspect ratio has to be superior to 10, which is considered to be the minimum aspect ratio value for good strength transmission for any reinforcement [15]. Fibers often fracture because of surface imperfections. Making the diameter as small as possible gives the fiber less surface area and, consequently, fewer flaws that might propagate during processing or under a load. A long fiber is preferable. The ends of a fiber carry less of the load than the remainder of the fiber, consequently, the fewer the ends, the higher the load ability of the fibers [13].

The process employed to prepare the specimens also has a significant effect. For example, injection molded specimens generally yield a higher tensile strength value than compression molded specimens. Machining usually lowers the tensile and elongation values because of the small irregularities introduced into the machine specimen. Another important factor affecting the test results is the location and size of the gate on the molded specimens. This is especially true in the case of glass-fiber-reinforced specimens. A large gate located on top of the tensile bar will orient the fibers parallel to the applied load, yielding higher tensile strength. A gate located on one side of the tensile bar will disperse the fiber in a random fashion. This effect is shown in Fig. 14 [12] and examples of composite sample configurations at different fiber orientation angles are shown in Fig. 15 [16].

The orientation of the fibers could also change the strength and stiffness of the composite. The reinforcing fibers may be introduced into the matrix in a number of orientations. Short, randomly oriented fibers having a small aspect ratio are easily introduced into the matrix and give relatively good isotropic behavior to the composite.

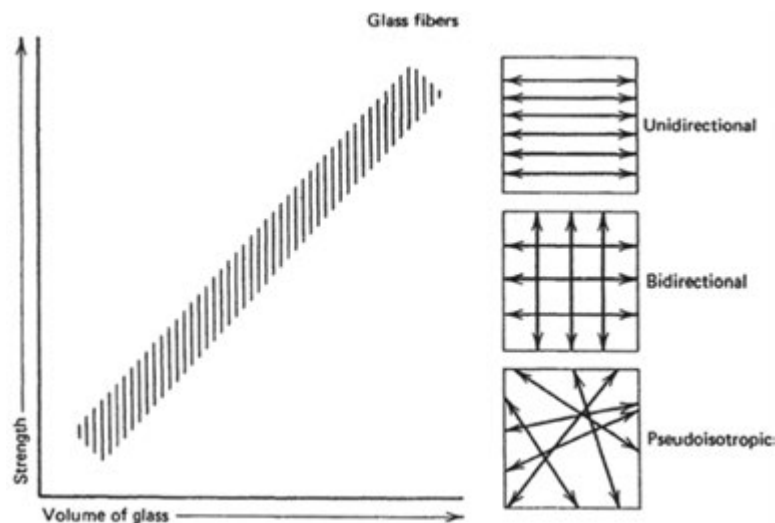


Fig. 14 The effect of fiberglass orientation [12].

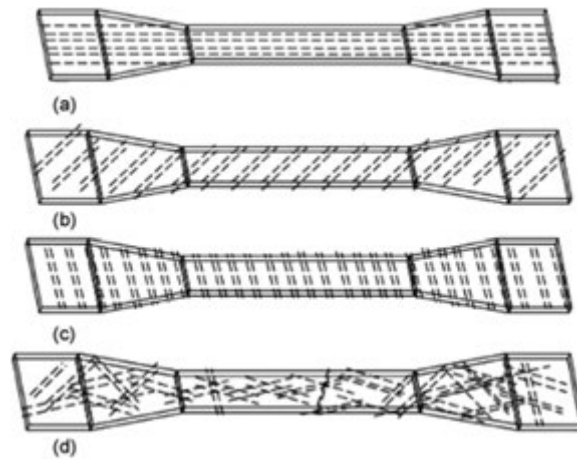


Fig. 15 Examples of composite sample configurations at different fiber orientation angles for tensile testing (a) 0° (b) 45° (c) 90° , and (d) random [16].

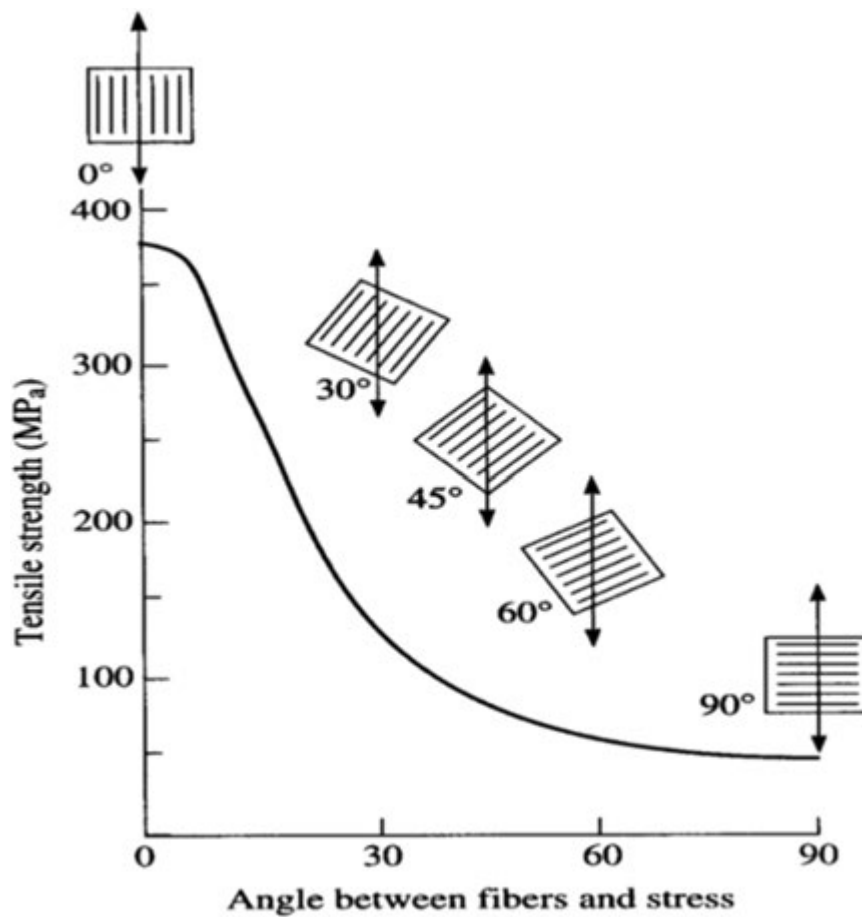


Fig. 16 Effect of fiber orientation on the tensile strength of an FRP composite [13].

Long or even continuous unidirectional arrangements of fibers produce anisotropic properties, with particularly good strength and stiffness parallel to the fibers. These fibers are often designated as 0° , indicating that all of the fibers are aligned with the direction of the applied stress. However, unidirectional orientations provide poor properties if the load is perpendicular to the fibers as in Fig. 16 [13].

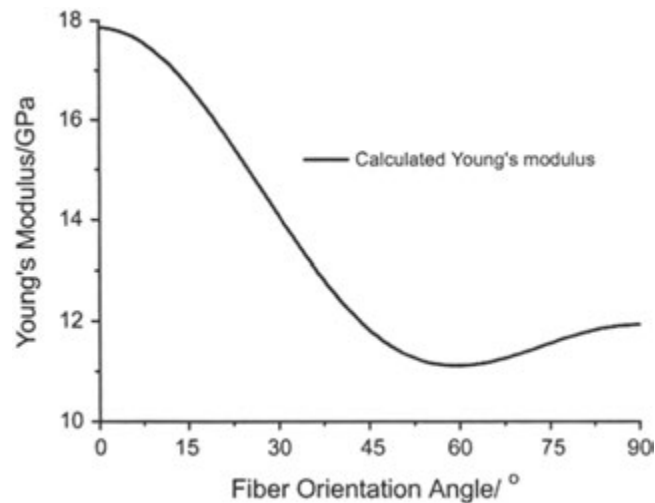


Fig. 17 Relationship between the composites' Young's modulus and fiber orientation angle (0° means along the fiber direction and 90° means perpendicular to the fiber direction) [17].

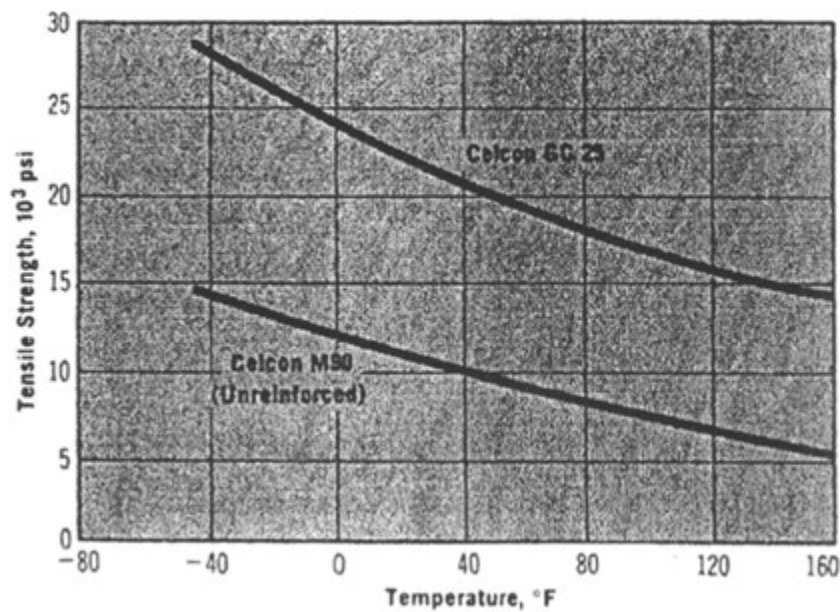


Fig. 18 The effect of temperature on tensile strength [12].

Fig. 16 shows that the greatest strength is obtained when the force is applied along the fibers and the least is when the force is applied perpendicular to the fibers [13].

In addition, the fiber orientation also effects the Young's modulus as in Fig. 17 [17].

From Fig. 17, it can be seen that the Young's modulus of the composites strongly depends on the fiber orientation angle. When the angle is 0° (loading along the fiber direction), the stiffness of the composites reaches its highest value. The lowest stiffness is when this angle is around 60° . After this angle, the composite's Young's modulus increases slightly with the rise of the fiber orientation angle.

Rate of straining

As the straining rate is increased, the tensile strength and modulus increase. However, the elongation is inversely proportional to the strain rate [12].



Fig. 19 Preparation of glass fiber with 45° orientation.



Fig. 20 Glass sheet cleaning.

Temperature

The tensile properties of some plastics change rapidly with a small change in temperature. Tensile strength and modulus are decreased while elongation is increased as the temperature increases. The effect of temperature on tensile strength is shown in [Fig. 18](#).

Materials and Methods

Preparation of Woven Fabric Glass Epoxy Composite Laminate by the Hand Layup Technique

The woven glass fibers were cut with 45° orientation as in [Fig. 19](#). A glass sheet was used at the top and bottom in order to obtain a good surface for the laminate. Initially, the glass sheet was cleaned 3 times to eliminate dust and avoid the sticking of the laminate after curing as in [Fig. 20](#). The fibers were stacked layer by layer upto 8 layers. A bonding agent (epoxy resin) was applied to create bonding between 8 layers of sheets, in the ratio of fiber:resin; 30:70. The resin was formed from two different chemicals. These were referred to as the 'epoxy' and the 'hardener'. The chemicals were mixed in the ratio of epoxy: hardener; 2:1. Each layer of the resin was poured onto the fiber uniformly to obtain the required bonding. The composites were then cured at room temperature overnight. The covering sheet (glass sheet) was placed and compressed as in [Fig. 21](#). After the curing process, the composites were

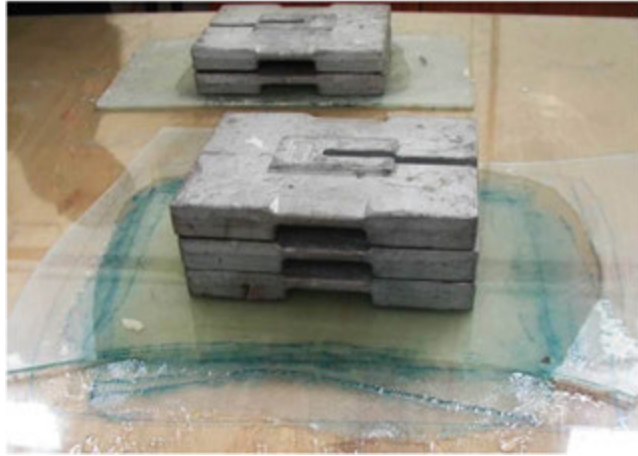


Fig. 21 Curing process.

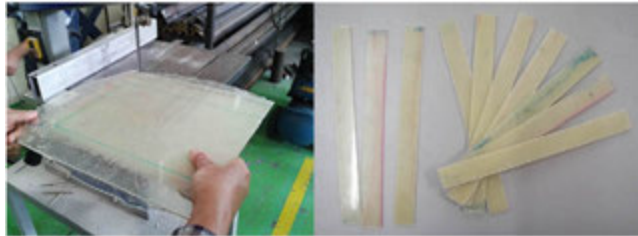


Fig. 22 Sample cutting.

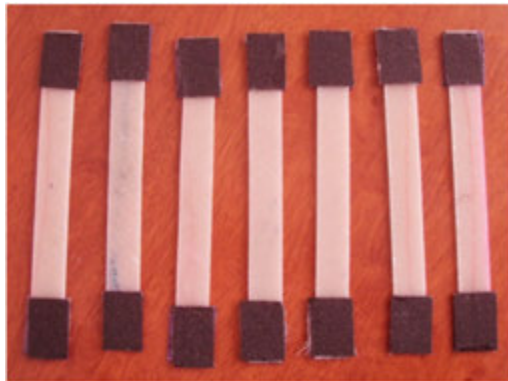


Fig. 23 Test specimens.

cut using a band saw with dimensions of 250 mm $\times$ 25 mm to the required size and shape according to ASTM D 3039/D 3039 M [18] as in Fig. 22. Thickness was also measured to calculate the cross-sectional area.

Mechanical Testing

The specimens were tabbed with sandpaper and were subsequently measured for gage length as in Fig. 23. The tensile properties of the composites were measured using a Galdabini Universal Testing Machine. Each tensile test was performed at a cross-head speed of 2 mm min⁻¹ on the specimens, until tensile failure was detected as in Fig. 24. Six specimens of sample were tested.

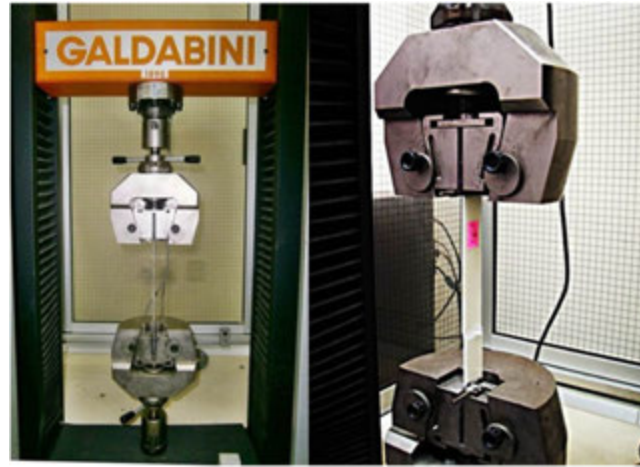


Fig. 24 Tensile testing fixture.

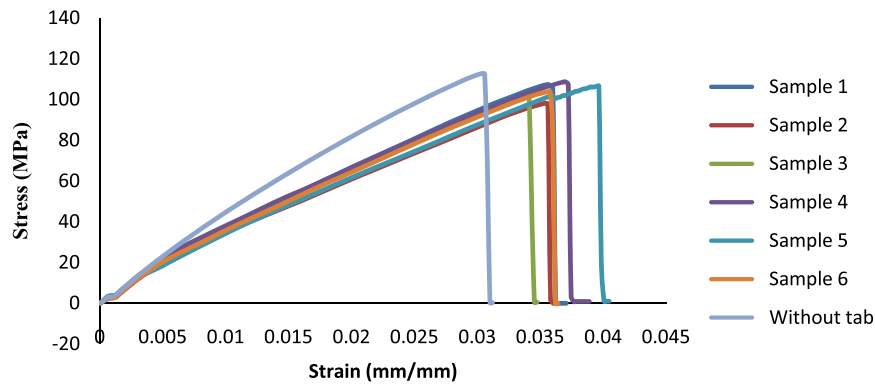


Fig. 25 Stress-strain curve of composite laminate with 45° orientation.

Data analysis

The load applied and the deflection were recorded. A stress and strain curve was plotted. The Young's modulus, the modulus of toughness (area under the stress-strain curve) and the percentage elongation at break point were also calculated as follows. The data was compared with the 60 and 90° orientation samples.

$$\sigma = F/A \quad [3]$$

where: σ =stress (Pa); F =load (N), and A =cross-sectional area (m^2)

$$\varepsilon = \Delta l/l \quad [4]$$

where: ε =strain; Δl =change in length (deformation), and l =gage length.

Results and Discussion

Effect of Fiber Orientation on Tensile Testing

Fig. 25 and **Table 2** illustrate the properties of the composite laminate of 45° orientation. Six specimens were tested and compared with the specimen without tab. A recent study found that the properties of specimens are affected by tabbing. More load is required for the fracture of the specimen without tab, and also more tensile strength and Young's modulus are obtained. Toughness is related to the area under the stress-strain curve. In order to be tough, a material must be both strong and ductile [12]. Therefore, the specimen with tab is stronger than the specimen without tab, because tab is required to prevent gripping damage during tensile testing [18].

Table 2 Comparison of properties of composite laminate 45° orientation between 'with tab' and 'without tab'

Properties	With tab	Without tab
Width (mm)	24.30	24.42
Thickness (mm)	2.68	2.62
Area ($E-05 \text{ m}^2$)	6.51	6.40
Gage length (mm)	160	160
Max load (KN)	6.78	7.15
Max deflection (mm)	5.96	4.99
Max stress (MPa); ultimate tensile strength (UTS)	104.25	112.711
Max strain (mm mm^{-1})	0.0372	0.0312
Young's modulus (Gpa)	4.516	5.081
Modulus of resilience (Kpa)	1.334	1.494
Modulus of toughness (Mpa)	2.12	1.93
Elongation at break (%)	3.71	3.12

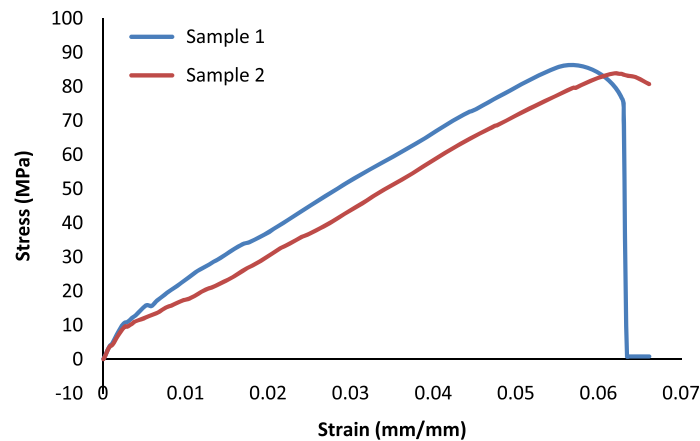
**Fig. 26** Stress-strain curve of a composite laminate with 60° orientation.

Fig.s 26 and **27** show the stress-strain curves of composite laminates with 60° and 90° orientation, respectively. Based on ASTM D 3039/D 3039 M, the number of specimens for tensile testing is at least five per test condition, unless valid results can be obtained through the use of fewer specimens. In a recent study, at degrees of 60° and 90°, the number of specimens tested was more than five, but only two specimens of 60° and three specimens of 90° were tested until tensile failure was detected. Meanwhile other specimens lost from grip or tab were loosened due to not enough glue being used for tab, or the fixture of the specimen with the machine not being fastened properly. Other configurations that have reportedly been successfully have incorporated steel tabs or tabs made of the same material as is being tested [18].

Moreover, **Fig. 27** demonstrates that the tensile strength of composite laminate sample 3 decreased during testing (as marked with a black circle). This can be a result of the lamination stage, which used a hand layup technique. So air bubbles occurred during this stage or the matrix phase (resin) did not disperse as well. Therefore, to prevent air bubbles from forming, a rolling device should be used.

It can be seen from **Table 3**, **Fig.s 28** and **29** that: (1) the maximum load, the ultimate tensile strength (UTS), the Young's modulus, and the modulus of toughness are highest in the case of 90° orientation. On the other hand, the maximum load and ultimate tensile strength are lowest in the case of 60° orientation, and the Young's modulus and also the modulus of toughness are lowest in the case of 45° orientation; (2) the maximum deflection is highest in the case of 60° orientation and led to maximum strain and elongation at break.

According to theory, the highest tensile strength obtained should be a composite with 0° orientation and the lowest with 90° orientation. This is because composites with 0° orientation possess long and continuous glass fibers to resist and transfer the tensile force, whereas the other fiber orientation angles (30°, 45°, 60°, and 90°) contain short, broken and discontinuous fibers [13, 16, 19]. But a recent study found that the highest tensile strength was obtained when the composite had a 90° orientation, which is in contrast with the theory described. However, there were a few research studies that

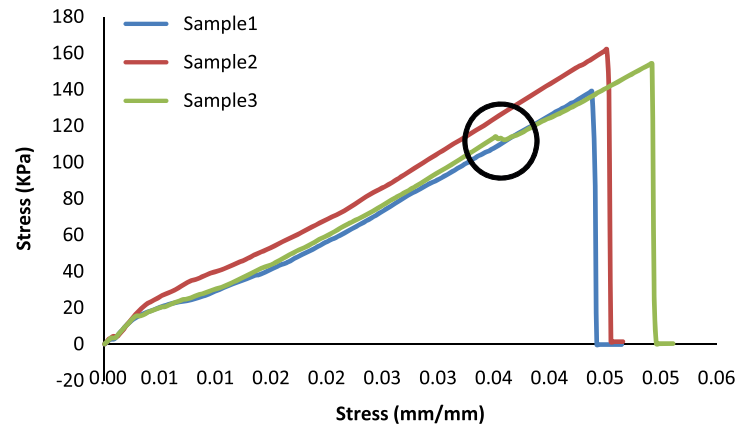


Fig. 27 Stress-strain curve of a composite laminate with 90° orientation.

Table 3 Properties of woven fabric glass epoxy composite laminate with different orientation

Properties	Orientation (°)		
	45	60	90
Width (mm)	24.30	25.75	25.09
Thickness (mm)	2.68	2.26	2.45
Area (E-05 m ²)	6.51	6.14	5.80
Gage length (mm)	160	160.5	160
Max load (KN)	6.78	4.96	9.33
Max deflection (mm)	5.96	10.61	7.68
Max stress (MPa); ultimate tensile strength (UTS)	104.25	85.14	151.66
Max strain (mm/mm)	0.0372	0.0661	0.0480
Young's modulus E (Gpa)	4.516	4.898	5.63
Modulus of resilience (Kpa)	1.334	2.45	1.27
Modulus of toughness (Mpa)	2.12	3.24	3.48
Elongation at break (%)	3.71	6.61	4.46

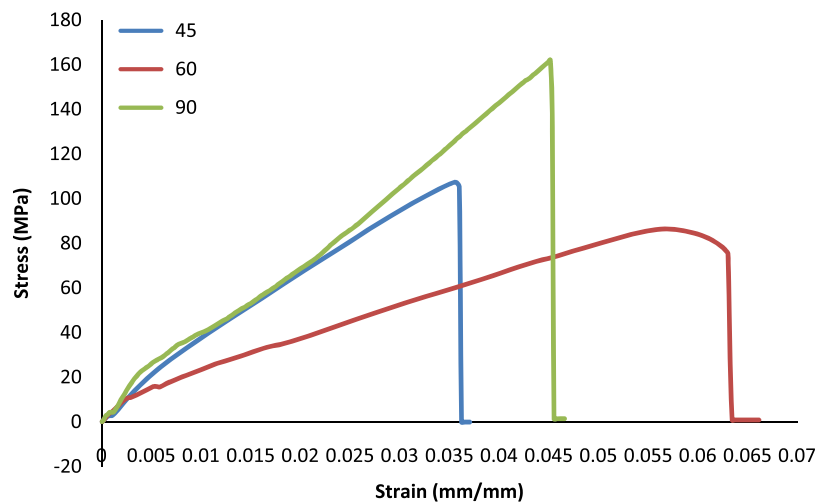


Fig. 28 Effect of fiber orientation on tensile strength.

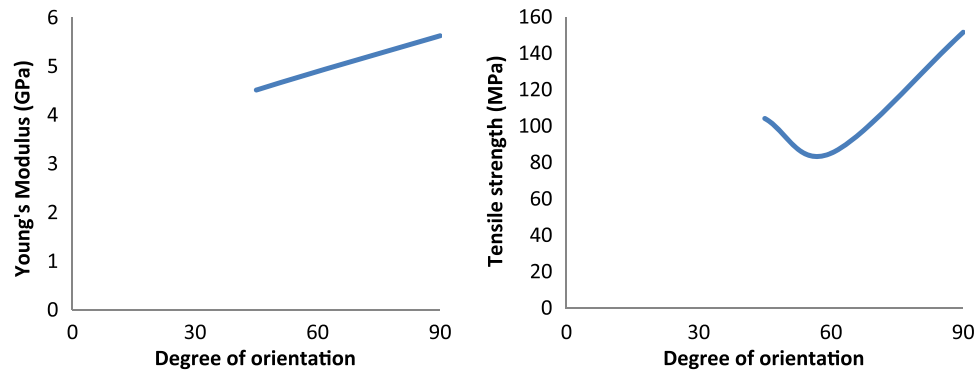


Fig. 29 Relationship between fiber orientation and (a) Young's modulus and (b) Tensile strength.

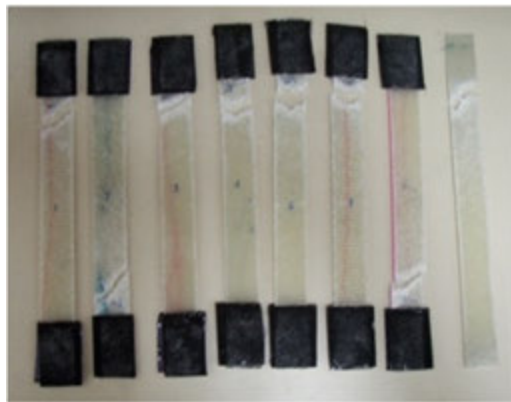


Fig. 30 Fractured specimen after tensile testing.

First Character		Second Character		Third Character	
Failure Type	Code	Failure Area	Code	Failure Location	Code
Angled	A	Inside grip/tab	I	Bottom	B
edge Delamination	D	At grip/tab	A	Top	T
Grip/tab	G	<1W from grip/tab	W	Left	L
Lateral	L	Gage	G	Right	R
Multi-mode	M(xyz)	Multiple areas	M	Middle	M
long. Splitting	S	Various	V	Various	V
eXplosive	X	Unknown	U	Unknown	U
Other	O				

Fig. 31 Tensile test failure codes/typical modes [18].

reported that the tensile strength will be affected by the resin content [20]. Since, in this study, a hand layup technique was used without a roller device for lamination, this may be the cause of the difference in resin content during the curing process even though the composite laminate was prepared using the same ratio of fiber: resin; 30:70. This subsequently had an effect on the tensile strength.

In addition, the theory of the relationship between the composites' Young's modulus and the fiber orientation angle indicates that the U-shaped dependency of the Young's modulus of the composites on the fiber orientation angle will be obtained when the angle is 0° (loading along fiber direction), and the stiffness of the composites then reaches its highest value. The lowest stiffness is when this angle is around 60° [17]. A recent study found that the lowest Young's modulus occurs in the case of 45° orientation. The result obtained is almost similar to the theory of the U-shape as shown in Fig. 29(b).

Failure Analysis

Fig. 30 demonstrates the failure of the specimens. Each specimen was tested until tensile failure was detected. It was found that some specimens fractured at the top, meanwhile some specimens fractured at the bottom. This may be affected by the different loads applied during manual fixing of the specimen with the instrument.

According to the tensile test failure codes as in Fig. 31, it can be concluded that there are two attributes of failure from this study – AGT and AGB – where A means the failure type is angle, G means the failure area is gage, T means the failure location is top, and B means the failure location is bottom.

Conclusion

In this work, woven fabric glass epoxy composite laminate was prepared using a hand layup technique and the effect of fiber orientation on the mechanical properties was investigated. The experiment found that:

(1) the maximum load, the ultimate tensile strength (UTS), the Young's modulus and the modulus of toughness are highest in the case of 90° orientation. On the other hand, the maximum load and the ultimate tensile strength are lowest in the case of 60° orientation, and the Young's modulus and also the modulus of toughness are lowest in the case of 45° orientation;

(2) the maximum deflection is highest in the case of 60° orientation and led to maximum strain and elongation at break. Therefore, to achieve the optimum property for future application, the manufacturing process should pay attention to the fiber orientation due to this being an important factor affecting the properties. From the design standpoint, the most significant properties can be categorized under the following three headings: strength, stiffness, and ductility.

Acknowledgment

The researchers would gratefully like to acknowledge the financial support given by the Universiti Putra Malaysia for this research.

References

- [1] Jain, R., Lee, L., 2012. Fiber reinforced polymer (FRP) composites for infrastructure applications focusing on innovation. In Technology Implementation and Sustainability. New York: Springer.
- [2] Thakura, V.K., Thakura, M.K., 2014. Processing and characterization of natural cellulose fibers/thermoset polymer composites. Carbohydrate Polymer 109, 102–117.
- [3] Chen, J., Zhao, D., Jin, X., *et al.*, 2014. Modifying glass fibers with graphene oxide: Towards high-performance polymer composites. Analytica Chimica Acta 97, 41–45.
- [4] Jeon, J., La Saponara, A.V., 2013. Thermal stress and deformation analyses in fiber reinforced polymer composites undergoing heat conduction and mechanical loading. Composite Structures 111, 31–44.
- [5] Kiran Kumar, P., Raghavendra, N.V., Sridhara, B.K., 2011. Optimization of infrared radiation cure process parameters for glass fiber reinforced polymer composites. Materials & Design 32 (3), 1129–1137.
- [6] Patel, S.U., Kulkarni, P.S., Patel, S.U., Chase, G.G., 2013. Glass fiber coalescing filter media augmented with polymeric submicron fibers and modified with angled drainage channels. Separation and Purification Technology 120, 230–238.
- [7] Mazumdar, S.K., 2002. Composites Manufacturing; Materials, Product, and Process Engineering. USA: CRC Press.
- [8] Miller, E., 1996. Introduction to Plastics and Composites: Mechanical Properties and Engineering Applications. New York: Marcel Dekker Inc.
- [9] Güneri, A. (Ed.), 2001. Handbook of Composite Fabrication. iSmithers Rapra Publishing.
- [10] Rosato, D.V., Rosato, D.V., 2004. Reinforced Plastics Handbook, third ed. Oxford: Elsevier Advanced Technology.
- [11] Craig Jr, R.R., 2000. Mechanics of Materials, second ed. New York: John Wiley & Sons.
- [12] Shah, V., 2007. Handbook of Plastics Testing and Failure Analysis, third ed. New Jersey: John Wiley & Sons.
- [13] Salar Bagherpour, 2012. Fibre Reinforced Polyester Composites. Available at: <http://www.intechopen.com/books/polyester/fibre-reinforced-polyester-composites> (accessed 19.10.15).
- [14] Knops, M., 2008. Analysis of Failure in Fiber Polymer Laminates. New York: Springer.
- [15] Bourmaud, A., Pimbert, S., 2008. Investigations on mechanical properties of poly (propylene) and poly (lactic acid) reinforced by miscanthus fibers. Composites: Part A 39, 1444–1454.
- [16] Tungjitpornkull, S., Sombatsomporn, N., 2009. Processing technique and fiber orientation angle affecting the mechanical properties of E-glass fiber reinforced wood/PVC composites. Journal of Materials Processing Technology 209, 3079–3088.
- [17] Wang, H.W., Zhou, H.W., Gui, L.L., Ji, H.W., Zhang, X.C., 2014. Analysis of effect of fiber orientation on Young's modulus for unidirectional fiber reinforced composites. Composites: Part B 56, 733–739.

- [18] ASTM, 2008. Standard test method for tensile properties of polymer matrix composite materials. ASTM D3039/D3039M, Annual Book of ASTM Standards, American Society for Testing and Materials.
- [19] Kumar, K.V., Reddy, P.R., Shankar, D.V.R., 2003. Effect of angle ply orientation on tensile properties of bidirectional woven fabric glass epoxy composite laminate. *International Journal of Computational Engineering Research* 3 (10), 55–61.
- [20] Green, M.A., Farooq, M.U., Lazzara, C.J., 2010. Resin to Fiber Ratio-Maximizing Tensile Properties in a Water-Activated, Polyurethane/Carbon Fiber Composite Repair System. Available at: <https://getinfo.de/app/Resin-to-Fiber-Ratio-Maximizing-Tensile-Properties/id/BLCP%3ACN078205725> (accessed 19.10.15).

Tensile Properties of Woven Intra-Ply Carbon/Kevlar Reinforced Epoxy Hybrid Composite at Sub-Ambient Temperature

Nurain Hashim, Dayang LA Majid, Danish M Baitab, Noorfaizal Yidris, and Rizal Zahari, University Putra Malaysia, Serdang, Selangor Darul Ehsan, Malaysia

© 2019 Elsevier Inc. All rights reserved.

This is a reproduction of Nurain Hashim, Dayang L.A. Majid, Danish M. Baitab, Noorfaizal Yidris, Rizal Zahari, Tensile Properties of Woven Intra-Ply Carbon/Kevlar Reinforced Epoxy Hybrid Composite at Sub-Ambient Temperature, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2019, doi:10.1016/B978-0-12-803581-8.11567-X.

Introduction

Hybrid composite materials were developed by the motivation of improving the imbalance properties of common homogeneous composite materials. From recent review done by Wu *et al.* [1] it was stated that hybrid composites can be considered to have positive hybrid effect on mechanical properties (e.g., failure strain, strength and impact properties) and fatigue strength resulted with improvement from its relative homogeneous composite. Previously, researches had been extensively investigated the mechanical properties and fatigue properties of different types of hybrid composites [1–4].

Carbon/Kevlar hybrid composite is one of hybrid composites that had been used widely in the commercial aircraft structures. It was proven in the previous works [5–7] that there were positive hybrid effect on its mechanical properties and fatigue behaviour. Although many studies had been done extensively on the mechanical properties of this hybrid composites at ambient temperature, investigations on the changes of these properties at low temperature are still lacking. Due to the weather condition, FRP composites applied in aircraft structures generally experience wide range of temperature changes during its operation [8,9]. Thus it is also necessary to identify the properties of these FRPs against the temperature changes to ensure its reliability to be exploited in the industry, especially the aircraft industry.

In non-ambient temperature, temperature changes can affect the materials' mechanical behaviours in many different ways such as thermoelasticity, displacement, strain, stress and other constitutive relations like elasticity related stresses or strain. Change in temperature generally will displace the materials' molecule structures by any general or relative motion and eventually will change the mechanical properties (stress distribution and strain) of the whole materials. These so called expansion and contraction in dimensions caused by the molecular bonds in materials to the changes of temperature is known as Coefficient of Thermal Expansion (CTE). The CTE value of a material presents how much strain it experiences for 1°C temperature change and if the material experience contraction instead of expansion, negative value of CTE will be obtained.

Due to its lower melting point, polymeric-based matrix is generally known as the most temperature-sensitive constituents in composite materials. With lowering of temperature, the energy of the molecular bonds decreased and leads to stiffening, resulting in increased hardness and brittleness. Similarly, reinforcing fibres also experience changes in molecular structures with change in environment temperature. Kevlar fibres showed expansion at fibre direction and contraction at transverse directions of the unit cells at low temperature [10–12]. In addition, it was also reported that Kevlar fibres's residual crystallinity, which was said to be closely related to the tensile modulus also changed to the changes of temperature [11]. Although the results reported that its residual crystallinity increases linearly as the temperature decreases, there was only a slight reduction of residual crystallinity between the ambient and 0°C temperature range, indicating that its tensile modulus might be lower at this temperature range. Even though the relationship between the residual crystallinity and tensile modulus was not reported in details as there was no experimental or analytical results discussed in this work, it was reported in work by Katogi *et al.* [13] that flexural strength and modulus of carbon composites increased as the crystallinity of its polypropylene matrix increased.

Regardless of the linear pattern of the individual matrices and fibres' dimension change to the temperature, the pattern in composites will not be in a linear manner. Non-linearity of expansion and contraction were found in several composite materials as reported by Reed and Golda [12]. Unidirectional CFRP and aramid FRP were generally will expand axially and contract transversely at low temperature. Meanwhile for matrices used in the composite materials reviewed, it contracted more than expansion and contraction experienced by the fibres at low temperature.

The big difference of expansion/contraction amount between the fibres and matrices at the same low temperature also can be represented as the mismatch of CTE. The larger mismatch of CTE at low temperature might cause the residual stresses at fibre-matrix interfaces to increase. Increased residual stresses then will possibly tend to enhance micro cracking in matrices and reduce the composite strength. This work then recommended using fibres with higher contraction rate like glass fibres for composite materials applied at low temperature range. Other than mismatch CTE induced residual stresses, composites mechanical behaviours at non-ambient temperature are also influenced by the thermal stresses [10,14]. As an example, Gates *et al.* [14] explained that total stress experienced by a UD composite laminate is the accumulation of both mechanical stresses and thermal stresses as shown in Eq. (1)

$$\begin{Bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \end{Bmatrix} = [Q] \left[\begin{Bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{12} \end{Bmatrix} - \begin{Bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{12} \end{Bmatrix}^T \right] \quad (1)$$

In this equation, Q is the value of the stiffness of the matrix, ε is the normal strain and thermal strain can be calculated from the equation below. From the equation, normal strain ε and shear strain γ can be obtained from the CTE values, α . The ΔT value in this equation is the temperature difference of the environmental testing temperature with the environmental temperature of the laminate at stress free condition during cure. This equation showed that larger value of CTE and temperature difference ΔT will result in a larger thermal strain.

$$\begin{Bmatrix} \varepsilon_{11}^T \\ \varepsilon_{22}^T \\ \gamma_{12}^T \end{Bmatrix} = \begin{Bmatrix} \alpha_1 \\ \alpha_2 \\ 0 \end{Bmatrix} \Delta T \quad (2)$$

It was also reported that nonlinear CTEs were obtained for composite materials at low temperatures, indicating that the stiffness and strength also varied with indiscernible pattern. An example is the work done by Gaitonde & Lowson [15] that showed the CTE value of carbon fibre composite (AS4/PEEK) can be plotted as 'U shape', where the CTE values are higher at very low temperature (-140°C) and at higher temperature (40°C). The lowest CTE was recorded at -80°C where it became brittle at this stage, but the composite materials went back to ductile state when the temperature kept decreasing. However, this non-linear pattern was only found in CFRP with unidirectional and angle-ply fibre arrangement. For CFRP with transverse fibre arrangement, its CTE value was found to be higher and changing linearly to the changes of temperature. It was concluded that the high expansion of the composite structures with transverse fibre arrangement was highly influenced by the matrix. Thus, it was recommended to conduct any low temperature mechanical testing at all temperature levels intended but with smaller range. Hence, the selection of temperature in this work lies within a small range between the ambient to -10°C whereas most reported works were conducted in the cryogenic region.

The mismatch of expansion and contraction between the fibres and matrices in composite structures also will significantly affect its mechanical properties under various stress conditions. From the results obtained by Hartwig & Knaak [10] compared to glass fibre composites, aramid fibres experienced larger contraction than its polymer matrix and caused the fibre-matrix interfacial bonding to decrease. At low temperature, the radial or transverse hydrogen bond in aramid fibres became stronger, reduced the adhesion and interfacial friction, and resulted with lower transverse and interlaminar shear strength compared to carbon and glass composite materials.

Aside from thermally induced effects on the mechanical behaviour, the configuration and arrangement of reinforcing fibre play a large role in influencing the tensile behaviour whereas the matrix has a dominant role in compressive behaviour. Reed and Golda [12] had previously reported on the positive effects on the tensile strength and modulus of unidirectional CFRP laminates at cryogenic temperatures. Much later, Sánchez-Sáez *et al.* [16] conducted tensile tests at discrete temperatures ranging from ambient to -150°C and showed that the tensile modulus slightly decreased for a cross-ply unidirectional CFRP but increased for a quasi-isotropic laminate. However, both configurations showed increase in tensile strength with decrease in temperature. Significant reduction in the failure strains at low temperatures was also reported. Their work concluded that the stacking arrangement was found to strongly affect the mechanical response. Meanwhile, Majerski *et al.* [8] reported the opposite where a decrease in tensile strength and increase of modulus for UD laminates at low temperatures was observed.

All the contradicting studies showed that the factors that influence the mechanical behaviour of composite materials at low temperature and their interactions cannot be readily estimated and therefore experimental investigation becomes necessary. The scope of the current work is on the investigations of the changes of tensile properties of woven intraply carbon/Kevlar hybrid composite at low temperature ranging from ambient to -10°C . A near ambient and small range of temperatures are selected to reduce the risk of encountering non-linear effects of thermal mismatch and relations between the temperature and tensile properties. The results were presented in tensile strength, tensile modulus and failure strain.

Methodology

The experimental work started with the preparations of the samples firstly by fabricating the composite laminates, followed by cutting and tabbing process as per the ASTM D3039-00. To characterize the properties of the fabricated hybrid composite materials, density test were conducted to determine the volume fractions of each of its constituents. Tensile test was conducted firstly at ambient temperature for obtaining ultimate tensile strength (UTS) and tensile modulus and failure strain of hybrid composites. Then tensile test was carried at lower temperature and properties were analyzed and compared to the data obtained from the tests done at ambient temperature.

Composite Plate Fabrication Using Vacuum Infusion (VI) Method

Vacuum Infusion (VI) process was used due to lower cost and ability to produce high quality composite materials that are suitable to be used in aircraft structures. The fabrication process of hybrid composite laminate started with preparing the materials and tools. Consistent with the application of the composite, which is to be used in mechanical testing, the right dimension of composite and required thickness are very important to be determined first. The details of the process and precautions done during fabricating woven carbon/Kevlar reinforced epoxy hybrid composite laminates also will be discussed in the next sub-topics.

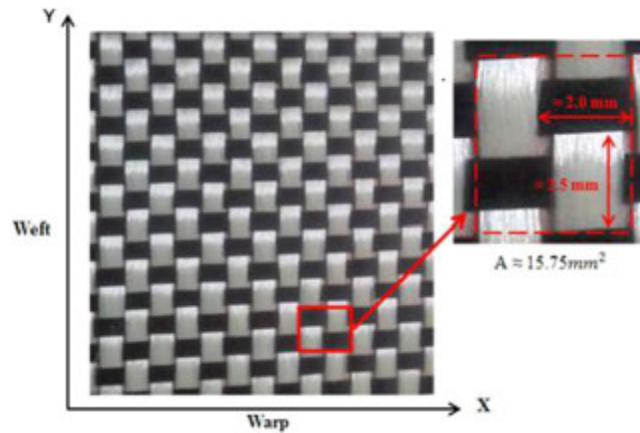


Fig. 1 Woven carbon/Kevlar cloth.

Table 1 Specifications of EpoxAmite 100 epoxy base resin with 103 slow hardener

<i>Handling properties</i>	
Specific gravity	1.108 g/cm ³
Mixed viscosity	650
Specific volume	9.1×10^{-4} m ³ /kg
<i>Physical properties</i>	
Ultimate tensile strength	54.54 Mpa
Tensile modulus	3.12 Gpa
Flexural strength	84.81 Mpa
Flexural modulus	2.96 Gpa
Compressive strength	72.39 Mpa
Heat deflection	53°C

Materials

(1) Reinforcing fibres

Fibres used in this work are composed of two different fibres, which are 3K carbon fibres and Kevlar-29. These two fibres were weaved together in one cloth, where carbon fibres as the warp and Kevlar fibres as the weft. One unit cell is the smallest repeating pattern in the woven cloth, where one unit cell of this woven cloth contains two unit cells of carbon fibre and two unit cells of Kevlar fibre. The area of one unit cell is approximately 15.75 mm² as shown in Fig. 1. The total fibre volume fraction, V_f is 60% and carbon fibre and Kevlar fibre ratio is 4:5. The thickness of the woven cloth is approximately 0.26 mm. For fabricating the composite plate, ten plies of fibre cloths with dimension of 300 mm × 500 mm and 350 mm and 500 mm were used.

(2) Matrix

The matrix of the composite was made of EpoxAmite 100 base epoxy resin, which a type of resin that can be cured in the room temperature. To accommodate the flow of resin and effectively infusing the fibre cloth, a slow hardening resin, the 103 type with low viscosity was used. The specifications of the resin can be found in Table 1, as given from the product's manufacturer. Slow hardener was chosen because of its longer curing time, which is 55 min. Longer time for the resin to cure allows it to be distributed uniformly during the infusion process. The hardener was used with mix ratio by weight of 100: 24 (resin:hardener).

Vacuum infusion manufacturing process

Vacuum infusion is utilized for the fabrication of the carbon/Kevlar reinforced epoxy hybrid composites. This process was chosen due to its ability to distribute the resin evenly without any excessive use of resin and work force. However, the drawbacks of this process are too many tools needed and without a proper control on the infusion pressure, decreased flow of resin will result in accumulation of resin at the center part of fibre lay-up. The overall flow of resin in vacuum infusion is visualized in a schematic

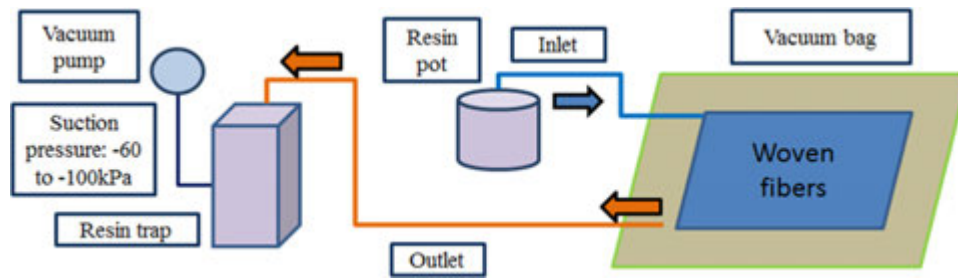


Fig. 2 Schematic diagram of the resin flow in a vacuum infusion process.

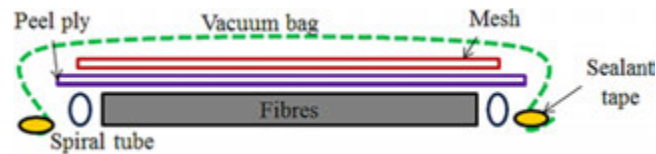


Fig. 3 Schematic diagram of arrangement of the open mold.

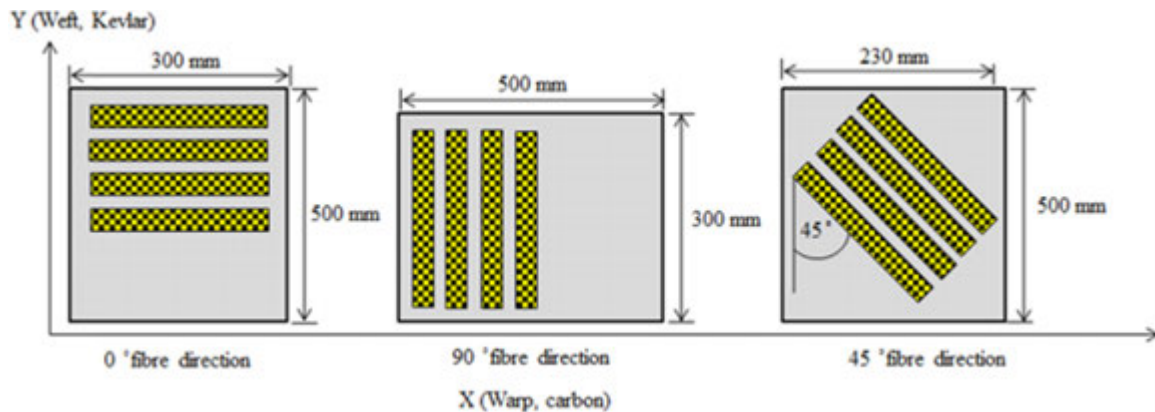


Fig. 4 Composite laminates dimensions and sample's cutting direction for tests at ambient temperature.

diagram in Fig. 2. The resin flow started from the resin pot to the open mold prepared through an inlet tube. The resin will flow the other end of open mold, where an outlet tube connecting the mold to the resin trap and vacuum pump.

The fabricating process was started with preparing the open mold for the composite plate. The arrangement of the open mold can be referred to the diagram showed in Fig. 3. Fibre layers were cut based on the required sample sizes stated in ASTM D303900 (25 mm × 250 mm) for both tensile and fatigue testing. Composite laminates sizes were optimized based on the sample's dimension and its fibre direction to avoid excessive waste of fibres as shown in Fig. 4.

To prevent the finished composite laminate to be bonded on the fabricating surface, moulding wax was applied at least three times before laying up the fibre layers. At both ends of the fibre layers were placed spiral tubes (Fig. 5(a)). These tubes were used to ensure that the resin enters and wet the fibre layers not only at one spot but also through the whole length of fibre layers. Then, a peel ply that works as the barrier between the laminate was laid up first on the fibre cloth (Fig. 5(b)). This ply allows the finished composite laminate to be peeled off from the vacuum bag easily. It is very important to make sure that the peel ply used is big enough to cover the fibre cloths and spiral tubes. A mesh sheet, which works to accelerate the resin flow and distribute the resin evenly inside the fibre cloths then placed on the peel ply. Finally, the laminate was covered and sealed with vacuum bag tightly (Fig. 5(c)). The outlet tube connected to the vacuum pump and this is where the vacuum pressure will be applied during the fabrication process (Fig. 5(d)).

After the vacuum bag was tightly sealed, resin infusion process will be started by turning on the vacuum pump to check any occurrence of leaks. The leaks should be checked using the leak detector. The resin infusion process was initiated with low pressure, around -30 kPa for several minutes. This step was done to observe any leaks and also to remove any air trap between the fibre layers.

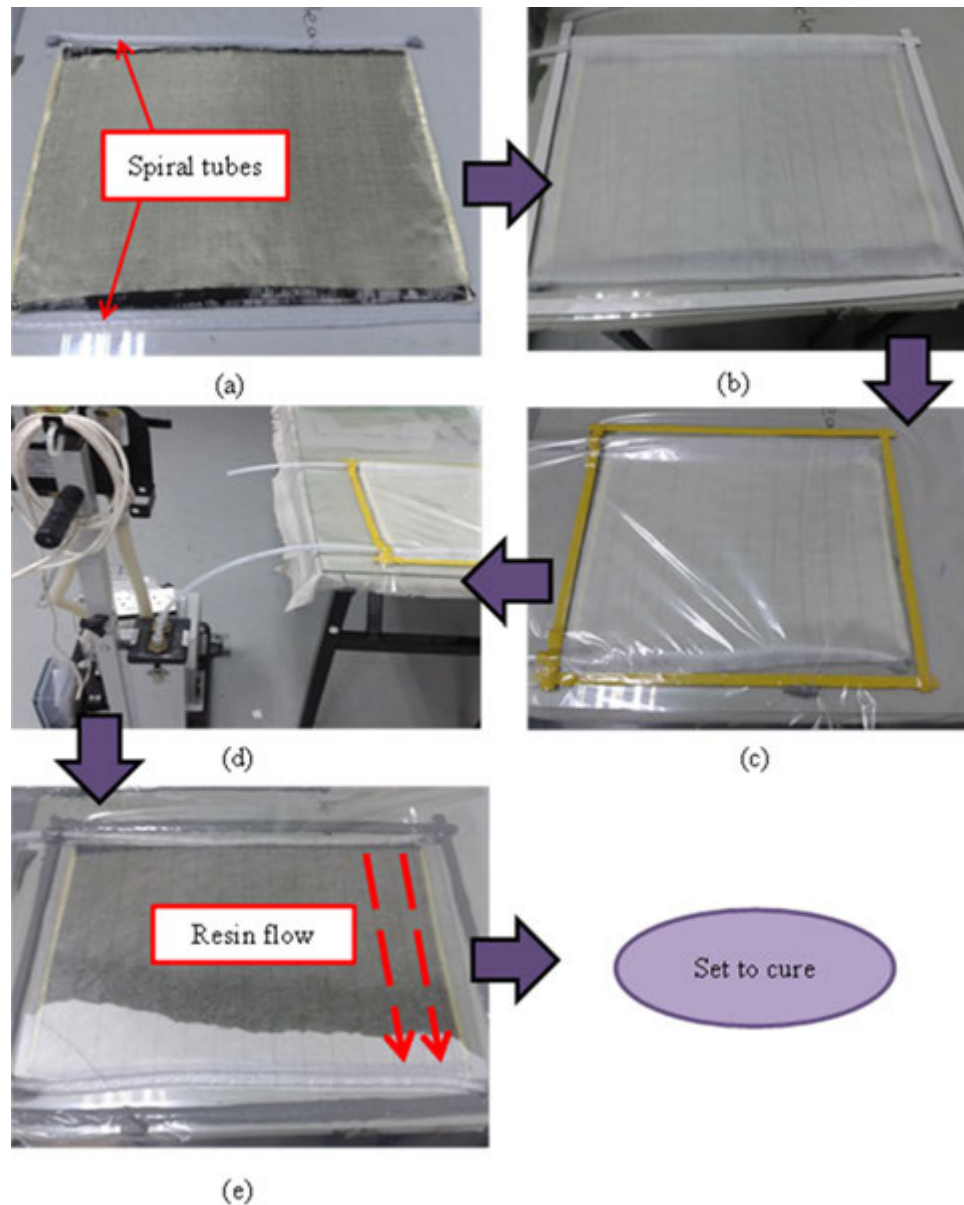


Fig. 5 Overall process of fabricating composite laminate by Vacuum Infusion method.

Then, the pressure was increased to -60 kPa and resin proceeded to infuse the cloth from the inlet tube. When the resin was already distributed midway of the fibre cloths, the pressure again was increased to -80 kPa and the resin gradually will flow until it reach the spiral tube at the other end of the fibre cloths (**Fig. 5(e)**). During this time, the resin flow is much slower and the pressure is increased to -100 kPa. When all the resin was completely infused into the fibre clothes, both inlet and outlet tube of the laminate were closed tightly and the laminates were set to cure in room temperature for 24 h in vacuumed condition.

After the composite laminate was fully cured, vacuum bag, peel-ply and mesh sheet were removed and the finished products were weighed whereby the final weight of the composite laminate is used to calculate the weight fraction and volume fraction of each constituents of the composite (fibres and matrix).

Tensile Testing

For tensile testing, the composite plates were cut into rectangular coupon shape with dimensions of 250 mm in length and 25 mm in width, according to the ASTM D3039. The thickness of all the specimens ranges from 2.0 to 2.3 mm. To avoid any slipping occurrence or failures at the grip area, 50 mm long emery cloths were attached at both ends of the top and bottom surface of the specimen. Tensile tests were conducted in accordance to ASTM D3039 using the MTS 810 universal tensile machine with the

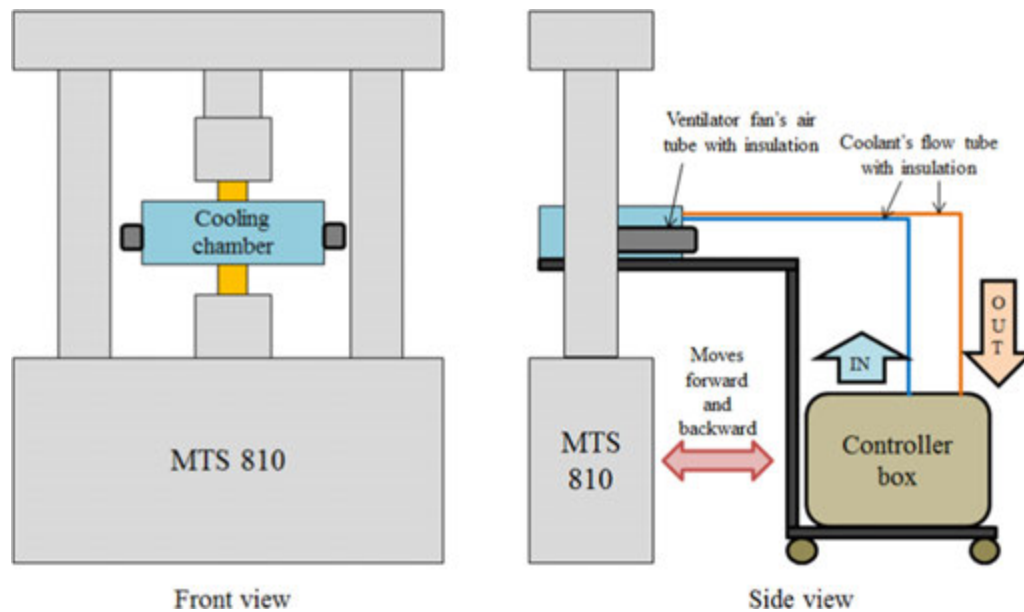


Fig. 6 The overall design of the cooling chamber system.

Table 2 Tensile properties of woven intraply carbon/Kevlar hybrid composites at ambient and low temperature

Test temperature [$^{\circ}\text{C}$]	Ultimate tensile strength, UTS [Mpa]	Tensile modulus, E [Gpa]	Poisson's ratio	Elongation at break (mm)
Ambient	554 ± 26.9	54.95 ± 1.67	0.1	6.31 ± 0.1
0	627 ± 3.19 (+ 13.2%)	50.73 ± 0.4 (− 7.7%)	0.1	4.2 ± 0.1 (− 33.4%)
− 5	652.73 ± 15.5 (+ 17.8%)	55.51 ± 1.03 (+ 1.0%)	0.1	4.14 ± 0.5 (− 34.4%)
− 10	592.23 ± 15.61 (+ 6.9%)	53.32 ± 1.11 (− 3.0%)	0.1	3.87 ± 0.2 (− 38.7%)

crosshead speed of 2 mm/min. Kyowa foil-type strain gauges were employed to measure the axial and lateral strain. For sub-ambient tensile tests, a customized cooling chamber was designed to provide the cool ambience needed (Fig. 6). The cooling chamber was designed with a through hole in the middle and cooling coils placed around the cooling box. The specimens were gripped and placed inside the through hole, which makes only the gage section of the specimens will be cooled inside the cooling chamber. Cooling coils were placed at both sides and back part of the cooling box to give the optimized cooling rate. Ventilation fans that placed at both side play the roles to circulate the air inside the cooling box and help the temperature of the air to be constant longer. The size of the cooling box was made to accommodate enough space between the two grips so that it will not collide with the grips during the cyclic loading. The cold environment was set to three temperatures, which were 0°C , -5°C and -10°C .

Results and Discussions

The mechanical properties obtained from the tensile tests at ambient and low temperatures was tabulated in Table 2 and compared with the materials' properties obtained from the tests done at ambient temperature. From the previous section, most reported works are on unidirectional composite laminates and conflicting findings have been reported. However, generally the strength increases while the modulus decreases due to reduced ductility.

From the results obtained, the tensile strength of the hybrid composite increased at all low temperature tested. Change of tensile strength and tensile modulus at ambient and low temperatures is shown in Fig. 7. This result was found to be in contrary with the results obtained in the previous work by Majerski [8] but in agreement with those obtained from reference [16]. Majerski [8] reported that as the matrix became brittle, the UTS of UID carbon fibre/epoxy composite decreased significantly at sub-zero temperature. However, the changes in the pattern is indiscernible as the increment of tensile strength at lowest temperature (-10°C) showed the least value compared to the other temperature but this could be due to within the bounds of experimental measurement uncertainties. These results showed that there is possibility that extended deformations of the brittle matrix took

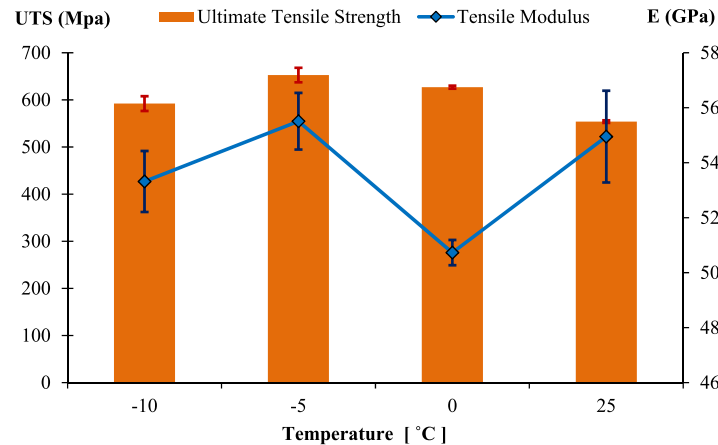


Fig. 7 Change of tensile strength and tensile modulus at ambient and low temperatures.

place at this state, thus resulting with reduced strength. The tensile modulus at 0°C, was found to be reduced significantly, which was 7.7% lower than its tensile modulus at ambient temperature. However, no significant changes were found for tensile modulus of the samples tested at -5°C and -10°C . On the other hand, composites' total elongation reduction can be seen for samples tested at all three different temperatures and the reduction increased as the temperature decreased.

Reduction of tensile modulus might be caused by the mismatch of thermal coefficient between fibres and matrix in the hybrid composite at lower temperature. This non-linear change of tensile modulus, which caused by the expansion and contraction of fibres at low temperature also had been reported to be found in several CFRP and Kevlar FRP [9]. In addition, Kevlar fibres crystallinity at low temperature might affect its tensile modulus as reported by Iyer *et al.* [11]. The results showed that residual crystallinity of Kevlar fibres was slightly reduced at 0°C and started to increase at sub-zero temperature (minimum -100°C). Thus, it explained that decreased crystallinity at 0°C caused the reduction of tensile modulus of hybrid composites investigated in this work. These results showed that colder environments generally delayed the softening process of the matrix and caused the composite materials to be able to sustain higher load. However, as the environmental temperature gets colder than 0°C, the matrix became more stiff and brittle. Stiffer matrix caused the composite materials to be more susceptible to abrupt failure, resulting with reduced strength. This brittle behaviour also can be seen from the high reduction of strain failure obtained from the test.

Conclusion

As a conclusion, intra-ply woven carbon/Kevlar hybrid composites have better tensile strength at near ambient low temperatures within a range of ambient to -10°C . Change of tensile modulus in hybrid composite to low temperature environment showed an indiscernible pattern, which might be caused by the mismatch shrinkage properties of the fibres and the matrix. On the contrary, the failure strain was seen to be decreased as the temperature decreased, showing that regardless of high strength it could sustain, stiffer matrix might affect the hybrid composite's impact resistance properties.

Acknowledgement

This work was fully supported by the School of Graduate Studies, Universiti Putra Malaysia with grant number 9463100.

References

- [1] Wu, Z., Wang, X., Iwashita, K., Sasaki, T., Hamaguchi, Y., 2010. Tensile fatigue behaviour of FRP and hybrid FRP sheets. *Composites Part B* 41 (5), 396–402.
- [2] Belingardi, G., Cavatorta, M.P., Frasca, C., 2006. Bending fatigue behavior of glass–carbon/epoxy hybrid composites. *Composites Science and Technology* 66 (2), 222–232.
- [3] Wan, Y.Z., Lian, J.J., Huang, Y., Wang, Y.L., Chen, G.C., 2006. Two-step surface treatment of 3D braided carbon/Kevlar hybrid fabric and influence on mechanical performance of its composites. *Materials Science and Engineering: A* 429, 304–311.
- [4] Fiore, V., Valenza, A., Di Bella, G., 2012. Mechanical behavior of carbon/flax hybrid composites for structural applications. *Journal of Composite Materials* 46 (17), 2089–2096.
- [5] Gustin, J., Joneson, A., Mahinfalah, M., Stone, J., 2005. Low velocity impact of combination Kevlar/carbon fiber sandwich composites. *Composite Structures* 69 (4), 396–406.
- [6] Wan, Y.Z., Wang, Y.L., He, F., Huang, Y., Jiang, H.J., 2007. Mechanical performance of hybrid bismaleimide composites reinforced with three-dimensional braided carbon and Kevlar fabrics. *Composites Part A: Applied Science and Manufacturing* 38 (2), 495–504.

- [7] Salehi-Khojin, A., Mahinfalah, M., Bashirzadeh, R., Freeman, B., 2007. Temperature effects on Kevlar/hybrid and carbon fiber composite sandwiches under impact loading. *Composite Structures* 78, 197–206.
- [8] Majerski, K., Surowska, B., Bienias, J., Pokojowej, N.I., 2012. Tensile properties of carbon fiber/epoxy laminates at low and room temperatures. *Polish Society of Composite Materials* 12 (3), 182–185.
- [9] Reed, R.P., Golda, M., 1994. Cryogenic properties of unidirectional composites. *Cryogenics* 34 (11), 909–928.
- [10] Hartwig, G., Knaak, S., 1984. Fibre-epoxy composites at low temperatures. *Cryogenics* 24 (11), 639–647.
- [11] Iyer, R.V., Sooryanarayana, K., Guru Row, T.N., Vijayan, K., 2003. Low temperature crystallographic data on Kevlar 49 fibres. *Journal of Materials Science* 38 (1), 133–139.
- [12] Reed, R.P., Golda, M., 1994. Cryogenic properties of unidirectional composites. *Cryogenics* 34 (11), 909–928.
- [13] Katogi, H., Takemura, K., 2014. The effect of crystallinity on the mechanical properties of plain woven carbon reinforced composites using polypropylene. *WIT Transactions on the Built Environment* 137, 301–310.
- [14] Gates, T.S., Whitley, K.S., Grenoble, R.W., Bandorawalla, T., 2018. Thermal/Mechanical Durability of Polymer-Matrix Composites in Cryogenic Environments 1, 1–12.
- [15] Gaitonde, J., Lowson, M.V., 1991. Low-temperature thermal expansion of PEEK, HTA and some of their composites reinforced with carbon fibres. *Composite Science and Technology* 40, 69–85.
- [16] Sánchez-Sáez, S., Gómez-del Río, T., Barbero, E., Zaera, R., Navarro, C., 2002. Static behavior of CFRPs at low temperatures. *Composite Part B: Engineering* 33 (5), 383–390.

Thermoplastic Composites for Fused Deposition Modeling Filament: Challenges and Applications

Kamaljit S Boparai, MRS Punjab Technical University, Bathinda, India
Rupinder Singh, Guru Nanak Dev Engineering College, Ludhiana, India

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Kamaljit S. Boparai, Rupinder Singh, Thermoplastic Composites for Fused Deposition Modeling Filament: Challenges and Applications, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2018, doi:10.1016/B978-0-12-803581-8.11409-2.

Introduction

FDM process has emerged as a revolution in the field of additive manufacturing (AM) where complex 3D structures can be fabricated quickly, without any assistance of conventional tooling, even at a low cost. FDM can generally be used for making models, prototypes, and also for batch production. The process starts from the identification of benchmark [1]. The FDM printed parts are also used for design validation, serviceability, and medical applications [2]. The reinforced ceramics in polymeric matrix have shown significant advantages [3,4]. Fig. 1 shows commonly used tests for thermal characterization of polymeric based composites. The reported literature highlights that the thermal stability of thermoplastic composites increased by increasing proportion of reinforcement, which needs to be explored systematically [5–8].

Sawpan *et al.* [8] conducted dynamic mechanical analysis (DMA) on glass fiber reinforced polymer to study the aging effect on its application, performance, and life time. The DMA detects the molecular motion changes in polymer composites with the variation of temperature. So far, mechanical characterization of polymer composite material is essential to choose the materials over traditional materials for numerous types of applications [9]. Essabir *et al.* [10] investigated the tensile and rheological properties of fibers reinforced composite, to realize the effect of fiber contents, frequency, temperature, and compatibilizer on the composite properties. Shanmugam and Thiruchitrambalam [11] studied the viscoelastic behavior of treated jute fiber and palm leaf stalk fiber reinforced in unsaturated polyester matrix. It has been observed that with the increase of fiber contents storage and loss modulus were enhanced and thus increases in both static and dynamic mechanical properties were observed.

The DMA provides information on polymeric material in dynamic state and is generally used to determine the stiffness and damping property of the material. The $\tan\delta$, (ratio of storage/loss modulus), is used as an estimate for damping properties [12]. Kumar *et al.* [13] reported the characterization of treated coconut sheath fiber reinforced epoxy composite (TCSE) and untreated (raw) coconut sheath fiber reinforced epoxy composite (UTCSE). The study concluded that the TCSE composite material possesses higher thermal stability and mechanical strength as compared with UTCSE. The DMA results indicate that the $\tan\delta$ curve of TCSE shifts toward higher temperature and lower peak as compared with UTCSE. This indicates that TCSE composite material has less damping effect and better load bearing capacity. Das and Satapathy [14] conducted DMA analysis on polypropylene (PP)/cenosphere based composite material and revealed that energy dissipation ability and storage modulus of 10 wt% of cenosphere composite material enhanced as compared with soft PP- phase. Stark [15] demonstrated the correlation of DMA and DSC results of carbon fiber fabric impregnated with reactive epoxy resin and indications were found for gelation and vitrification (transformation of a substance into glass). Jakobsen *et al.* [16] investigated the change in Young's modulus during the isothermal curing of chopped strand mat E glass/epoxy composite. In another study storage/loss modulus and glass transition temperature of fly ash and polyuria composites were increased and as the fly ash contents increased [17].

Ornaghi *et al.* [18] outlined the properties of glass hybrid composites through DMA testing. It was concluded that storage/loss modulus increased with the higher glass loading and overall fiber volume. Cho and Bahadur outlined DMA analysis on polyphenylenesulfide composites reinforced with carbon nanofiber [19]. No significant effect on the damping properties was observed with the reinforcement. Brostow and Lobland [20] established a connection between brittleness and wear of polymeric materials by DMA and sliding wear test. They developed a formula that predicts the percentage recovery in sliding wear from the brittleness of material. Sa'ude *et al.* [21] performed DMA of ABS material reinforced with copper and concluded that storage modulus and $\tan\delta$ increased proportional with the loading of copper. Arivazhagan and Masood [22] demonstrated the DMA results under the influence of temperature and

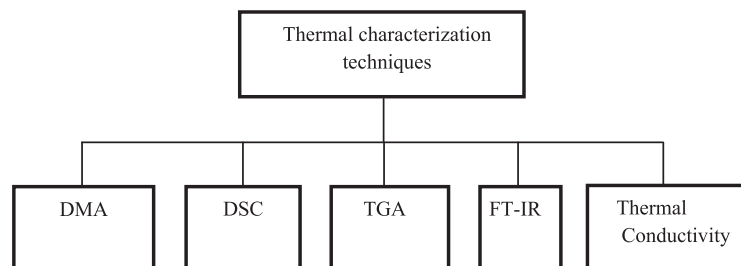


Fig. 1 Various techniques for the thermal characterization of polymeric based materials.

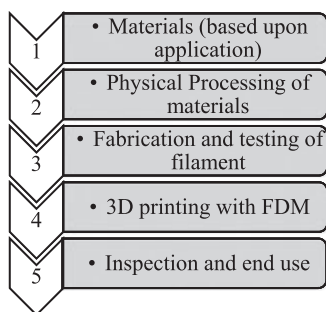


Fig. 2 Feedstock filament development process.

Table 1 Observations for MFI with different proportions

S No	Proportion (weight %)				MFI (g/10 min)
	ABS	E-35 Nylon 6	Al	Al ₂ O ₃	
1	100	–	–	–	2.415
2	–	100	–	–	10.61
3	–	70	30	–	6.825
4	–	60	40	–	3.975
5	–	50	50	–	2.375 ^a
6	–	80	–	20	6.995
7	–	70	–	30	6.53
8	–	60	–	40	2.44 ^a
9	–	50	–	50	1.855

^aMFI value of thermoplastic composite near to commercially used ABS material.

frequency of ABS specimens fabricated on FDM by varying input parameters such as raster angle and width and built style. The study highlights that loss modulus increases with temperature while viscosity decreases with temperature.

In this work, the step-by-step procedure for preparing Nylon6-Al-Al₂O₃ feedstock filament, in place of commercial ABS material, has been presented for FDM. The viscoelastic properties were also studied by DMA analysis.

Development of Composite Material Feedstock Filament

The detailed experimental study has been executed at Manufacturing Research Lab, GNDEC, Ludhiana, India for the development of this composite material, so that the application domain of FDM process can be increased. The Fig. 2 shows the feedstock filament development process.

For this case study E-35 grade (extrusion grade) Nylon 6 was selected as a matrix material. The material was procured from local market of average particle size 4–5 mm and milled to 500–800 µm with cryogenic milling at – 96°C. Commercially pure aluminum metal (Al) of 325 mesh size and aluminum oxide (Al₂O₃) of 100 mesh size were selected as reinforcement. The flow properties of thermoplastic composites are strongly influenced with reinforcement of fillers [23,24]. In this study, 10 observations were recorded for each composition/proportion (see Table 1) and the average value was selected for further processing. This limits the practical levels of reinforcement in the thermoplastic polymers.

As observed from Table 1, MFI of virgin ABS is 2.415 g/10 min and virgin Nylon 6 is 10.61 g/10 min. It has been observed that by 40% reinforcement of Al powder, its MFI is 3.975 g/10 min and by 50% reinforcement it reduces to 2.375 g/10 min. Similarly, for Al₂O₃, it is more suitable if the loading remains less than 40%. Finally in this study 40% reinforcement of filler materials in Nylon 6 was kept as fixed.

The various ingredients of composite material were heated in vacuum oven to 55°C for 9 h at perfect vacuum conditions. The reinforcement in polymer matrix was mixed in tumbler mixture at 200 rpm for 2 h.

Filament Fabrication with Extrusion Process

Flow characterization

For preparing spoolable material in form of feedstock, having required consistent diameter, the processing conditions of new filament material can be controlled, by deliberately selecting the contents of binder and fillers materials [24–27]. It has been reported that the reinforcement in E-35 Nylon 6 results in modification of material morphology [23,28–30]. Fig. 3(a) shows the setup with a cylinder (with

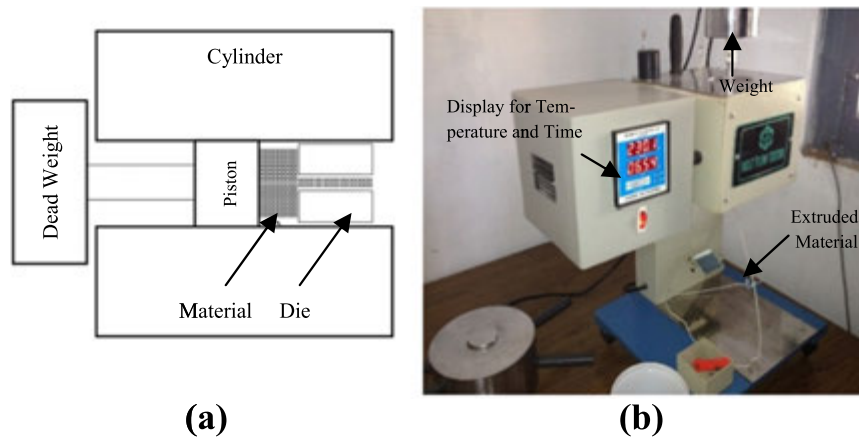


Fig. 3 MFI apparatus (a) Schematic of MFI setup; (b) Pictorial view of MFI setup.

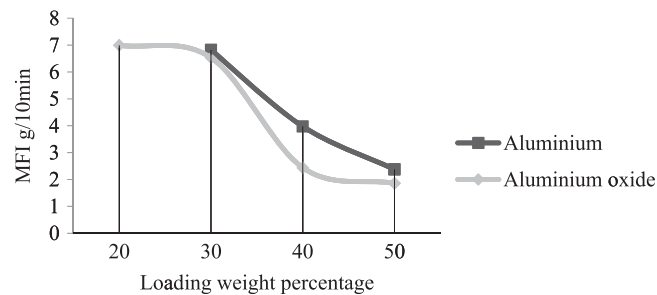


Fig. 4 Variation of MFI with reinforcement of Al and Al_2O_3 .

Table 2 Proportion (by weight) of binder and filler materials

Composition/ proportion	Nylon 6 (E-35)	Al powder	Al_2O_3 powder
A	60	26	14
B	60	28	12
C	60	30	10

temperature controlled circuit), piston, weights, and capillary die fitted at the bottom. The test has been conducted by maintaining cylinder temperature at 230°C and weight 3.8 Kg. **Fig. 3(b)** shows a pictorial view of the MFI tester. For each composition an average of minimum 10 observations were recorded. **Fig. 4** shows MFI values with reinforcement (of Al/ Al_2O_3) in various proportions.

Table 2 summarizes the proportions (by weight) of compositions/proportions. Based upon **Table 2**, MFI values are shown in **Fig. 5**. It has been observed that with increase of large particle sized (100 mesh) Al_2O_3 particles and decrease of small particle sized (325 mesh) Al in composition/proportion of polymeric composite, the MFI decreases. Moreover Al_2O_3 is ceramic material and its surface is rough, which may resist the particle mobility in the composite matrix.

Fabrication of filament with extrusion process

The actual single screw extrusion process is shown in **Fig. 6**. Further, **Table 3** shows the specifications of single screw extrusion process used in the present study. The critical input parameters for extrusion process are screw speed, exit die temperature, speed of take up unit, temperature of water tank, screw barrel temperature, and die nozzle diameter. Initially, the trials were performed and one set of parameters is selected that gives favorable responses such as uniform distribution of filler materials, desired filament diameter with minimum deviation and strength. **Table 4** shows input parameters for screw extrusion.

Inspection of feedstock filament

The qualification of newly processed feedstock filament for FDM process relies on various parameters such as material processing conditions required for fabrication of the filament, homogenous particle inclusion of filler in binder material, flow/rheological

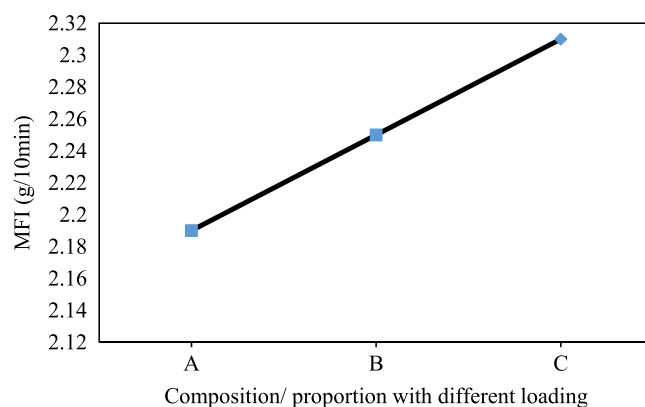


Fig. 5 MFI of various compositions/proportions.

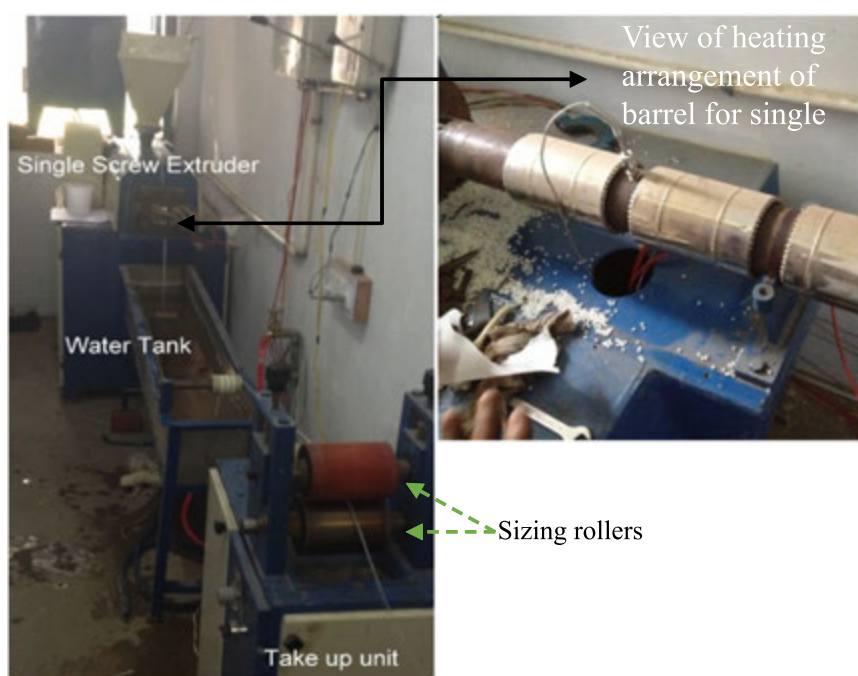


Fig. 6 3D view of extrusion process.

Table 3 Screw extruder specifications

Extruder Type	Screw diameter (mm)	L/D ratio	No of heaters		Speed of screw (rpm)	Take up unit rpm
			Barrel	Die		
Single Screw	25	26	3	1	0–40	0–40

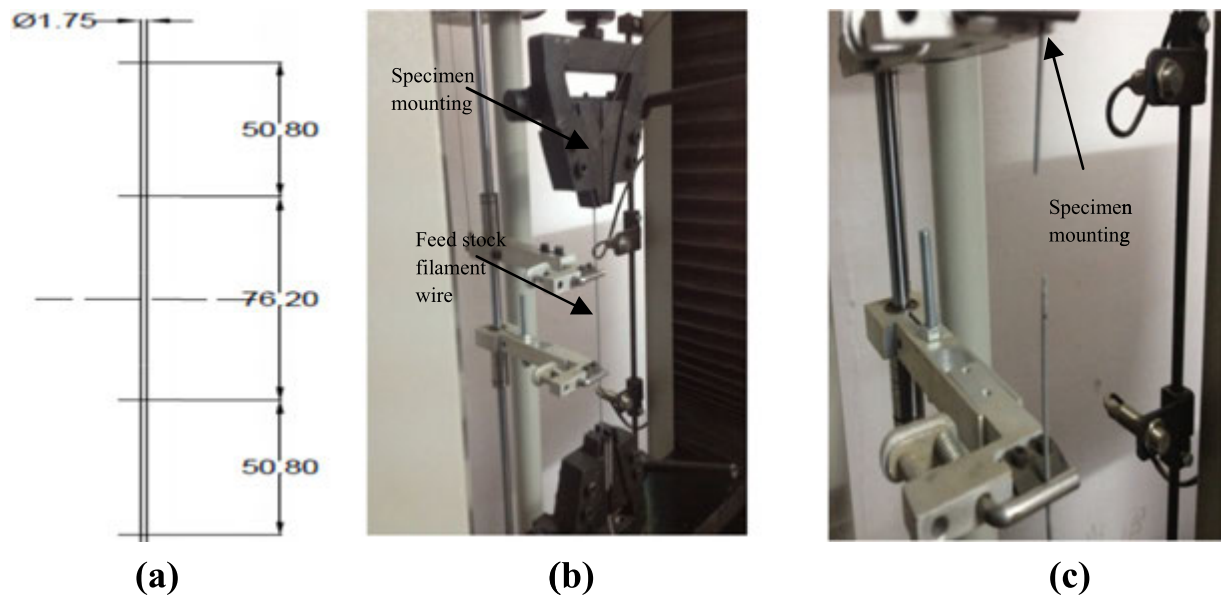
and adhesion characteristics of constituents. It should be noted that the fabricated filaments (Fig. 7(a)) were stored in a dry place, to prevent moisture from the atmosphere. The visual inspection of the filament diameter was performed with digital micrometer (see Fig. 7(b)). Finally, filament within the diameter range of 1.75 ± 0.03 mm was successfully fabricated.

Mechanical (Tensile) testing of feedstock

The tensile strength of newly prepared feedstock filaments was checked as per ASTM-638 standard. Fig. 8(a) shows standard dimensions of tensile testing sample. Fig. 8(b–c) shows the pictorial view of specimen before and after testing. For this testing, 5 samples from each specimen were measured and average value has been reported in Table 5.

Table 4 Extrusion input parameters

<i>Barrel temp</i>	<i>Die temp</i>	<i>Screw speed</i>	<i>Take up speed</i>	<i>Material</i>
				<i>Composition/proportion</i>
170	205	35	27	A/B/C

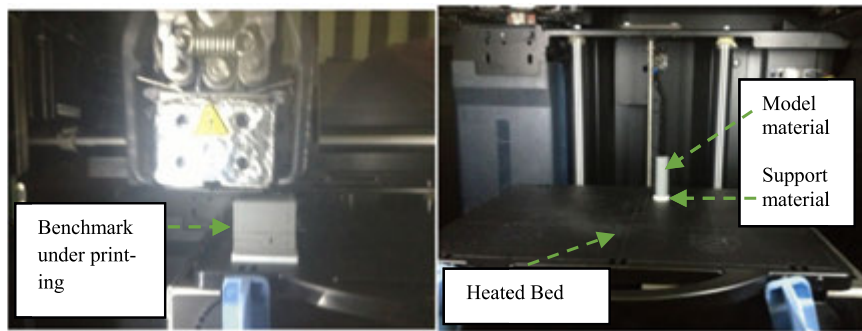
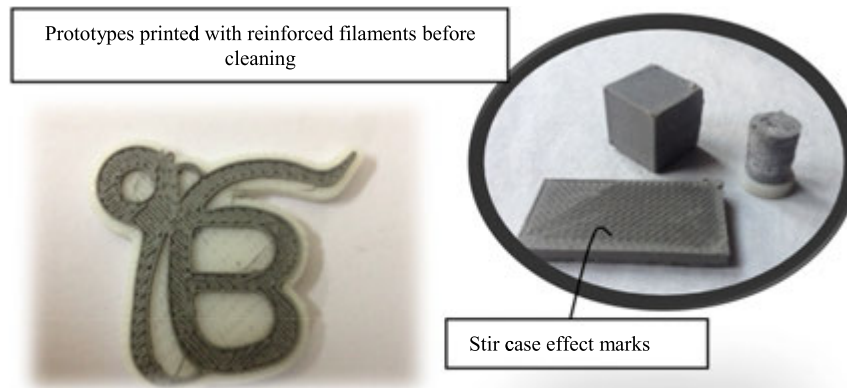
**Fig. 7** (a) Filament spool; (b) Visual inspection with micrometer.**Fig. 8** Tensile testing (a) standard specimen; (b) Sample held on UTM; (c) broken sample on UTM.

3D printing on FDM setup

For this study a u-PrintSE (Stratasys, USA) commercial FDM setup has been used. The wires of different compositions/proportions (as per Table 2) were run successfully on FDM. It should be noted that no buckling of wire was observed during plunging of filament, which indicates that the material is strong enough to force the material through the nozzle. However, it was also observed that the FDM nozzle got choked during the fabrication of parts (see Fig. 9). With increase in proportion of Al_2O_3 , the material gets clotted and it becomes difficult to pass through the liquefier head nozzle. Secondly, the increase of Al_2O_3 content in matrix causes increase in flow resistance. Since Al has self-lubricating properties and with the increase in its contents, it does not cause an abrasion effect on nozzle. Fig. 10 shows FDM printed parts.

Table 5 Observations for tensile testing

<i>Proportion</i>	<i>Tensile strength</i>	<i>Elongation at break</i>	<i>Young's modulus</i>
A	21.40 MPa	18.62%	582 MPa
B	21.53 MPa	12.74%	760 MPa
C	21.65 MPa	8.56%	1165 MPa
ABS ^a	22.0 MPa	6.0%	1627 MPa

^asupplier's data.**Fig. 9** Printing of parts on FDM.**Fig. 10** Final FDM prints.

Dynamic mechanical analysis

The DMA provides information on polymeric material in dynamic state and generally is used to determine the stiffness and damping behavior of the material [31]. The specimens for DMA analysis were fabricated with developed alternative material feedstock filaments on FDM setup. The rectangular shaped samples of $20 \times 9.5 \times 1.75$ mm for DMA analysis were prepared with solid density mode having raster angle $45^\circ/45^\circ$ (see Fig. 11).

The measurements for viscoelastic properties of developed composite materials and ABS material test specimens have been carried out in three-point bending mode. The tests were performed at a fixed frequency of 1 Hz and heating rate was $2^\circ\text{C}/\text{min}$ with a maximum dynamic force of 10 N. The specimens were initially dried in a vacuum oven at a temperature of 50°C for 8 h. The characterization includes storage modulus, loss modulus, and $\tan\delta$ for qualitatively and quantitatively investigating the effect of reinforcement in Nylon 6 matrix. Additionally, study highlights the shift of glass transition temperature and stiffness of composite materials.

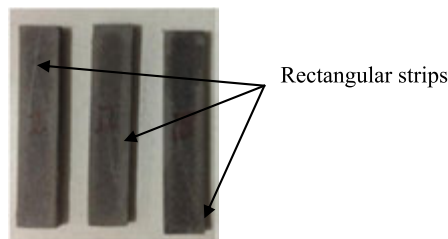


Fig. 11 FDM printed samples for DMA.

Discussion

Rheological Properties

The flow behavior study of selected compositions of Nylon 6-Al-Al₂O₃ was recorded as per ASTM D1238-73 standard. This was done to investigate the flow rate at processing temperature in extrusion liquefier head of FDM. It has been pointed out that the presence of filler material in the matrix of Nylon 6 increases its viscosity as compared with virgin Nylon 6. Moreover, viscosity also increases with an increase to the particle size of filler materials. The MFI value of Al and Al₂O₃ was plotted on weight percentage loading scale as shown in Fig. 4. The curve illustrates that, in Nylon 6 matrix, the loading for Al metal is possible up to 45% and in case of Al₂O₃, it is limited to 40%. These comparative results can predict the flow behavior of newly developed material and this data helps to select the composition most suitable for FDM. The reason is that this composition can be processed in same conditions as ABS material has during the processing in FDM system. It has been depicted from Fig. 5 that composition “C” has high MFI value (2.31 g/10 min) and composition A has the least MFI value (2.19 g/10 min). The flow behavior of composition “C” is almost the same as the ABS material has, under the same temperature and pressure conditions (ASTM D1238-73). If the flow rate increases past the desired value it causes improper building of the part model and adversely effects the surface texture/finish.

Tensile Properties

It has been realized that as the proportion and size of filler material in polymeric matrix increase, mechanical strength starts decreasing [13–15]. The effect of reinforced material in polymeric matrix on Young’s modulus is highlighted in Table 5. The result shows that Young’s modulus and tensile strength of newly developed materials are less than ABS material but its percentage elongation is more. This is mainly attributed to the weak interaction of metallic material with polymeric materials and formation of voids around metal particles inside the polymeric structure. The Young’s modulus and tensile strength have high values for ABS but its results show slight decrease in values for composite materials. Among selected compositions it shows increase in value with increase in Al content. Moreover, it should be noted that Al₂O₃ particle size is larger than Al metal. The elongation at break also shows significant change and increase with increase in filler content and particle size. It was estimated from the results that tensile strength of alternative material (composition “C”) filament has slightly lesser value than standard ABS filament but with this composition, no buckling of filament takes place at the entrance of extrusion liquefier head of the FDM system during 3D printing. Moreover the tensile strength decreases with the increase in weight proportions of Al₂O₃ particles. This is mainly attributed to the poor compatibility of Al₂O₃ material with binder material (due to its abrasive nature). The feedstock filaments of composition “A” and “B” showed frequent buckling. This is due to poor mechanical properties and it causes nozzle chocking during part production process. Finally, tensile testing of filament successfully determined the suitability/compatibility of alternative material filament for the FDM system.

Dynamic Mechanical Analysis

3.3.1 Viscoelastic behavior of composite materials

The viscoelastic behavior of three compositions of Nylon6-Al-Al₂O₃ was studied to investigate the change in glass transition temperature and stiffness of material at processing temperature in the liquefier head of the FDM system. The parameters such as storage modulus characterize the stiffness, loss modulus highlights the energy dissipated in one loading cycle, and loss factor ($\tan \delta$) represents the internal resistance or mechanical damping of the polymeric based materials.

Storage modulus (E')

The variations of storage modulus with temperature for composition A, B, and C are shown in Fig. 12. The higher value of storage modulus for composition C is due to the increase in intermolecular bonding resulting from the presence of larger weight % proportion of Al than Al₂O₃ in Nylon 6 matrix (as already mentioned, composition C contains 30% Al and 10% Al₂O₃ particles). Moreover, average particle size of Al and Al₂O₃ are 50 μm and 150 μm , respectively. Due to the large particle size of Al₂O₃, the increase of its weight % proportions of reinforcement in Nylon 6 matrix causes poor interfacial bonding as in the case of composition A and B. In addition to the above, Al metal has a self-lubricating property and higher thermal conductivity than

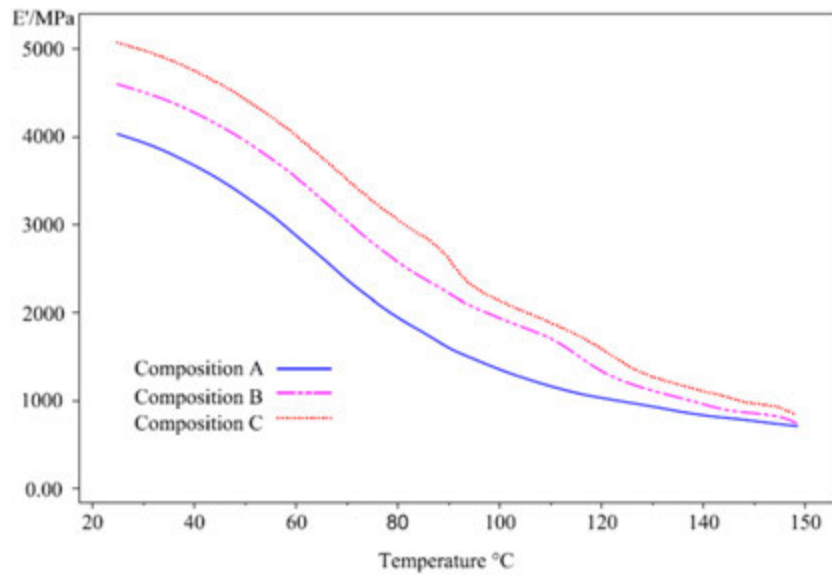


Fig. 12 Storage modulus curves vs. temperature.

Al_2O_3 . The higher reinforcement of Al causes better heat and stress transfer and retains better matrix adhesion. The higher value of storage modulus exhibits high stiffness, which shows that composition C has high stiffness as compared with composition A and B. It is noteworthy that the increase in storage modulus due to filler reinforcement is more noticeable in the rubbery region than the glassy region as compared with ABS material. As the storage modulus indicates the capacity of material to store the input mechanical energy, it decreases with the increase of temperature [25]. The storage modulus is generally used for determining elastic properties of a polymeric based material. The curves show that, initially at low temperature, the storage modulus has high value and with the increase of temperature its value decreases gradually. In the intermediate region of the curves, the transition from the glassy state or energy elastic state to rubbery state or entropy elastic state occurs. This region indicates the onset of chain mobility [25]. This trend remains the same for all the compositions and is due to reinforcement of filler materials in the matrix. At elevated temperature, the storage modulus drops, which exhibits loss of stiffness. Among various compositions, composition C has maximum value of storage modulus in rubbery region compared with other composites.

Loss modulus (E'')

The loss modulus highlights the viscous properties of a polymeric based material and represents energy lost as heat or dissipated during one cyclic load. Typical loss modulus curves of the abovementioned compositions as a function of temperature are illustrated in Fig. 13. It should be noted that loss modulus was approximately steady at low temperature and rises to peak value at the onset temperature, which indicates the maximum heat dissipated per unit deformation [9]. The loss modulus of composition A is higher followed by composition B and C. There are two explanations for the change in peaks of loss modulus with the variation in weight proportions of fillers. First, the spherical shape of filler materials can enhance the energy dissipation under the influence of dynamic load [18]. Secondly, the polymer metal slippage or filler particle–particle slippage are resisted at low temperature due to the difference of coefficient of thermal expansion of polymer and fillers. The particle–particle slippage dissipated more heat. As the amount Al_2O_3 in Nylon 6 matrix increases, the peak values of loss modulus increases. The high peak value of loss modulus indicates that the intermolecular bonding is destroyed [9]. Fig. 13 shows the effect of type of filler and amount of filler are found to influence more on the value of loss modulus above the temperature of high peak value [12]. The curve become broadens after peak value, which indicates the difference in physical state of matrix surrounding the filler materials (Al and Al_2O_3). The trend remains the same for all the compositions.

Assessment of Loss factor ($\tan \delta$)

The $\tan \delta$ (ratio of E''/E' as per ISO 6721-1 standard) versus temperature variations for the proportions A, B, and C have been recorded (Fig. 14). A high value of loss factor of a polymeric material signifies nonelastic strain component. The DMA determines not only damping or loss modulus, but is also suitable for glass transition temperature (T_g) measurements. As the change in modulus under the influence of temperature is much more noticeable in DMA than other techniques such as differential scanning calorimeter (DSC), so it is more suitable for T_g measurements. Although T_g can be evaluated from the peaks of loss factor and loss modulus it is easy to measure from the peak of loss factor (ASTM D 4065-2001). The glass transition temperature (T_g), for proportions A, B, and C was observed as 82.5°C, 87.6°C, and 93.5°C respectively. The $\tan \delta$ results highlight that the composition/proportion C has high stiffness followed by composition B and A, but all are acceptable for running on commercial FDM. It was observed while printing of samples for DMA that feedstock filaments prepared with composition/proportion B and C run

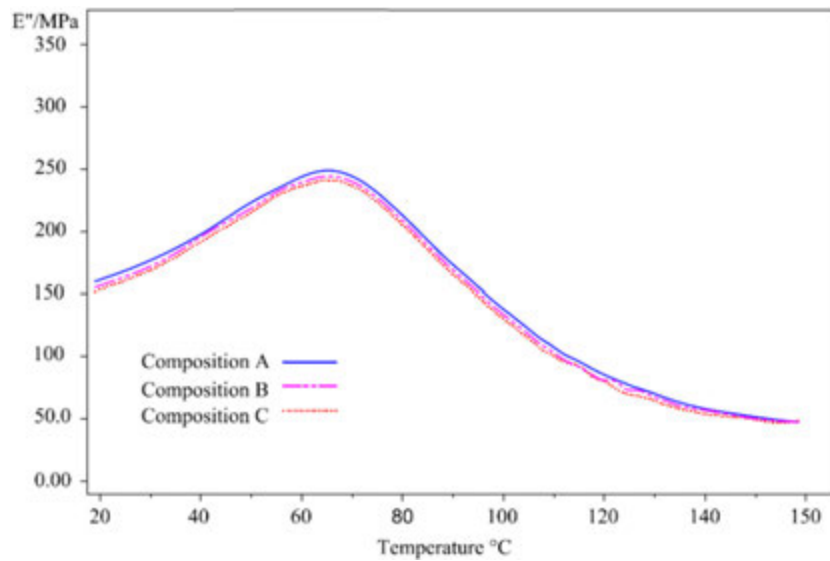


Fig. 13 Loss modulus curves vs. temperature.

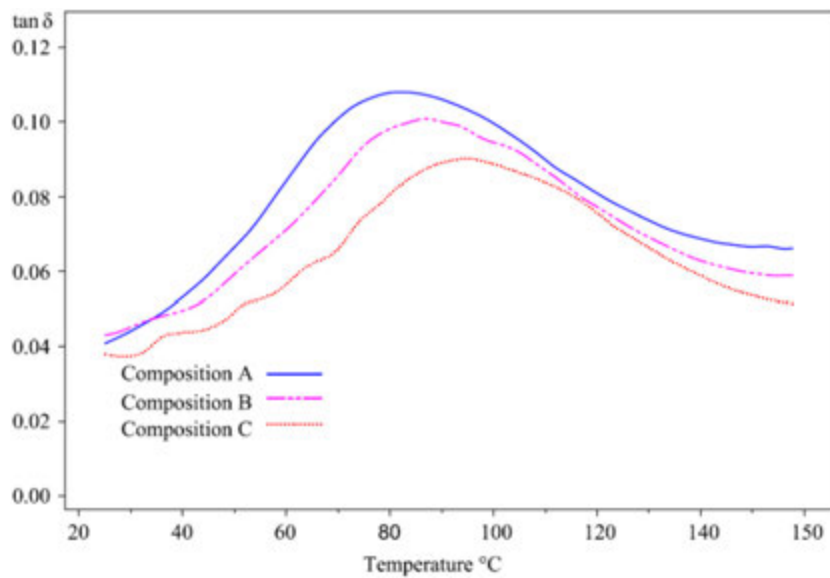


Fig. 14 Tan δ curves vs. temperature.

successfully without buckling in the FDM head. Whereas in composition/proportion A, the material buckled during the processing on FDM. The reason is due to large particle size and amount of Al_2O_3 filler particles in matrix. The reinforcement of filler material reduces the peak of tan δ curve [25]. With the filler reinforcement in Nylon 6 matrix, tan δ value decreases and T_g shows a shift toward higher value. The shifting of T_g toward higher temperatures indicates the decreased mobility of the chains with the reinforcement of fillers. The lowering of tan δ value indicates the improvement in interfacial bonding within the alternative material matrix [26,27]. So, it is ascertained that the alternative material "proportion C" has more stiffness and glass transition temperature than the proportions A and B.

Viscoelastic behavior of ABS material

Fig. 15 shows storage loss modulus and loss factor for ABS. As explained above, in the low temperature region, the material is in glassy state. However, in this region ABS material has storage modulus value less than alternative composite materials and this difference remains throughout the experimentation. In the transition region, the curve shows a rapid decrease in storage modulus to a constant value with the increase of temperature but composite material shows a gradual decrease in its value. This result indicates that ABS material has less stiffness than composite materials. The loss modulus and loss factor curves of ABS material

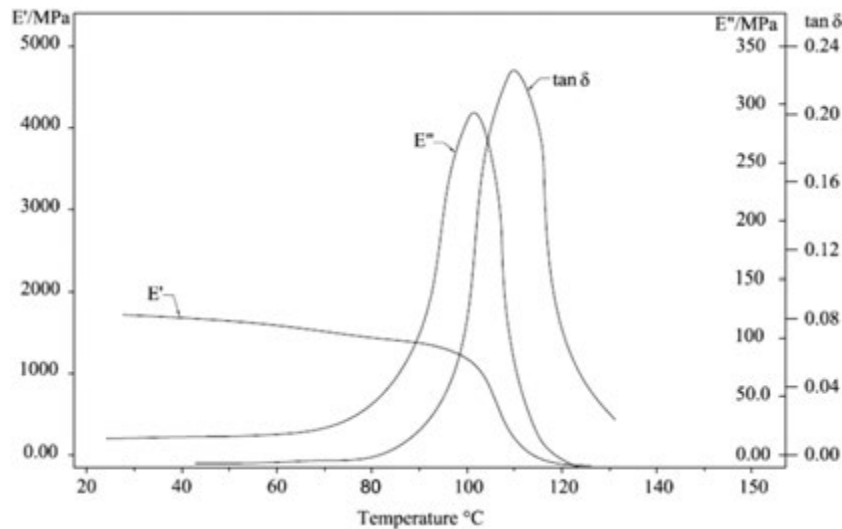


Fig. 15 DMA curves of ABS material.

exhibited higher peak value compared with those of composite materials. At temperature below glass transition, ABS material has lower loss modulus than those of composite materials and the intensity of the corresponding peak is also lower. For ABS, the glass transition temperature corresponding to $\tan \delta$ peak is 108°C and its peak value is 0.228, which is higher than composite materials. This is another reason that highlights low stiffness due to higher molecular mobility in ABS material.

From the above discussion it is realized that the composite materials possess better dynamic mechanical properties than standard ABS material.

Conclusions and Outlook

The experimental outputs are summarized as follows:

- (1) An alternate thermoplastic composite feedstock filament comprising of Nylon 6- Al_2O_3 has been successfully prepared for FDM. Based upon MFI analysis, 40% reinforcement in Nylon 6 matrix was established as a better solution in this case study.
- (2) Further for 40% reinforcement in Nylon 6 matrix, three proportions (A/B/C) were compared for tensile properties. The results of study suggests that the tensile strength of proportions A, B, and C are 64%, 53%, 28% poorer than ABS material, whereas tensile modulus is 2.7%, 2.1%, 1.5% lower than ABS material.
- (3) DMA of composition/proportion A, B, and C was performed and found better than ABS. In this case study the storage modulus for different selected compositions/proportions of reinforcements increases with the increase of filler amount in the Nylon 6. This resulted in a shift of glass transition temperature (toward the higher side). The increase of storage modulus highlights the good interfacial adhesion between polymer filler particles. Among various compositions, composition C has a rigid matrix.
- (4) The loss modulus curves, which are indicative of the dissipated energy (heat or stress) under cyclic load, were found to be shifted to higher position with the increase in Al_2O_3 content in the matrix. It has been observed that the composition/proportion A has the highest peak value followed by compositions B and C.
- (5) The glass transition temperature shifted toward the higher side with reinforcement of filler material in the matrix. This is because of constraints imposed on the mobility of molecules within the matrix. In case of composition C, the $\tan \delta$ curve shows a large shift toward the right side of the graph, which indicates the evidence of good interfacial bonding. $\tan \delta$ was found to be the lowest peak for composition C compared with compositions B and A.

References

- [1] Singh, R., 2013. Some investigations for small-sized product fabrication with FDM for plastic components. *Rapid Prototyping Journal* 19 (1), 58–63.
- [2] Nikzad, M., Masood, S.H., Sbarski, I., 2011. Thermo-mechanical properties of a highly filled polymeric composites for fused deposition modeling. *Materials & Design* 32 (6), 3448–3456.
- [3] Cucosa, A., Budruga, P., Miub, L., Mitrea, S., Sbarcea, G., 2011. Dynamic mechanical analysis (DMA) of new and historical parchments and leathers: Correlations with DSC and XRD. *Thermochimica Acta* 516 (1-2), 19–28.
- [4] Gabr, M.H., Phong, N.T., Okubo, K., *et al.*, 2014. Thermal and mechanical properties of electrospun nano-celulose reinforced epoxy nanocomposites. *Polymer Testing* 37, 51–58.

- [5] Luyt, A.S., Molefi, J.A., Krump, H., 2006. Thermal mechanical and electrical properties of copper powder filled low-density and linear low density polyethylene composites. *Polymer Degradation and Stability* 91 (7), 1629–1636.
- [6] Massood, S.H., Song, W.Q., 2004. Development of new metal/polymer materials for rapid tooling using fused deposition modelling. *Materials & Design* 25 (7), 587–594.
- [7] Mamunya, Y.P., Davydenko, V.V., Pissis, P., Lebedev, E.V., 2002. Electrical and thermal conductivity of polymers filled with metal powder. *European Polymer Journal* 38, 1887–1897.
- [8] Sawpan, M.A., Holdsworth, P.G., Renshaw, P., 2012. Glass transitions of hygrothermal aged pultruded glass fibre reinforced polymer rebar by dynamic mechanical thermal analysis. *Materials and Design* 42, 272–278.
- [9] Abdeen, M.A., 2012. Static and dynamic mechanical properties of poly (vinyl chloride) loaded with aluminum oxide nano powder. *Materials and Design* 33, 523–528.
- [10] Essabir, H., Elkhaoulani, A., Benmoussa, K., *et al.*, 2013. Dynamic mechanical thermal behavior analysis of doum fibers reinforced polypropylene composites. *Materials and Design* 51, 780–788.
- [11] Shanmugam, D., Thiruchitrabalam, M., 2013. Influence of alkali treatment and layering pattern on the tensile and flexural properties of Palmyra palm leaf stalk fiber (PPLSF)/ jute fiber polyester hybrid composite. *Composite Interfaces* 21 (1), 3–12.
- [12] Luo, X., Li, J., Feng, J., Yang, T., Lin, X., 2014. Mechanical and thermal performance of distillers grains filled poly (butylene succinate) composites. *Materials and Design* 57, 195–200.
- [13] Kumar, S.M.S., Duraibabu, D., Subramanian, K., 2014. Studies on mechanical, thermal and dynamic mechanical properties of untreated (raw) and treated coconut sheath fiber reinforced epoxy composites. *Materials and Design* 59, 63–69.
- [14] Das, A., Satapathy, B.K., 2011. Structural, thermal, mechanical and dynamic mechanical properties of cenosphere filled polypropylene composites. *Materials and Design* 32 (3), 1477–1484.
- [15] Stark, W., 2013. Investigation of the curing behaviour of carbon fibre epoxy prepreg by Dynamic Mechanical Analysis DMA. *Polymer Testing* 32 (2), 231–239.
- [16] Jakobsen, J., Jensen, M., Andreasen, J.H., 2013. Thermo-mechanical characterization of in-plane properties for CSM E-glass epoxy polymer composite materials – Part 2: Young's modulus. *Polymer Testing* 32 (8), 1417–1422.
- [17] Qiao, J., Amirkhizi, Q.J., A, V., Schaaf, K., Nemat-Nasser, S., 2011. Dynamic mechanical analysis of fly ash filled polyurea elastomer. *Journal of Engineering Materials and Technology* 133 (1), 011016 (1–7).
- [18] Ornaghi, H.L., Bolner, A.S., Fiorio, R., Zattera, A.J., Amico, S.C., 2010. Mechanical and dynamic mechanical analysis of hybrid composites molded by resin transfer molding. *Journal of Applied Polymer Science* 118 (2), 887–896.
- [19] Cho, M.H., Bahadur, S., 2007. A study of the thermal, dynamic mechanical, and tribological properties of polyphenylene sulfide composites reinforced with carbon nanofibers. *Tribology Letters* 25 (3), 237–245.
- [20] Brostow, W., Lobland, H.E.H., 2008. Predicting wear from mechanical properties of thermoplastic polymers. *Polymer Engineering and Science* 48 (10), 1982–1985.
- [21] Sa'ude, N., Masood, S.H., Nikzad, M., Ibrahim, M., Ibrahim, M.H.I., 2013. Dynamic mechanical properties of Copper-ABS composites for FDM feedstock. *International Journal of Engineering Research and Applications* 3 (3), 1257–1263.
- [22] Arivazhagan, A., Masood, S.H., 2012. Dynamic mechanical properties of ABS material processed by fused deposition modelling. *International Journal of Engineering Research and Applications (IJERA)* 2 (3), 2009–2014.
- [23] Singh Boparai, K., Singh, R., Singh, H., 2016. Experimental investigations for development of Nylon6-Al-Al₂O₃ alternative FDM filament. *Rapid Prototyping Journal* 22 (2), 217–224.
- [24] Mostafa, N., Syed, H.M., Igor, S., Andrew, G., 2009. A study of melt flow analysis of an ABS-Iron composite in fused deposition modelling process. *Tsinghua Science & Technology* 14, 29–37.
- [25] Masood, S.H., Song, W.Q., 2004. Development of new metal/polymer materials for rapid tooling using fused deposition modelling. *Materials & design* 25 (7), 587–594.
- [26] Wang, M., Wang, W., Liu, T., Zhang, W.D., 2008. Melt rheological properties of nylon 6/multi-walled carbon nanotube composites. *Composites Science and Technology* 68 (12), 2498–2502.
- [27] Shenoy, A.V., Saini, D.R., Nadkarni, V.M., 1983. Rheology of nylon 6 containing metal halides. *Journal of Materials Science* 18 (7), 2149–2155.
- [28] Ramanath, H.S., Chua, C.K., Leong, K.F., 2008. Melt flow behavior of poly-ε caprolactone in fused deposition modeling. *Journal of Materials Science: Materials in Medicine* 19, 2541.
- [29] Bellini, A., Shor, L., Guceri, S.I., 2005. New developments in fused deposition modeling of ceramics. *Rapid Prototyping Journal* 11 (4), 214–220.
- [30] Zhang, Y., Chou, Y.K., 2006. Three-dimensional finite element analysis simulations of the fused deposition modelling process. *Proceedings of the Institution of Mechanical Engineers Part B: Journal of Engineering Manufacture* 220 (10), 1663–1671.
- [31] Bose, S., Mahanwar, P.A., 2004. Effect of flyash on the mechanical, thermal, dielectric, rheological and morphological properties of filled nylon 6. *Journal of Minerals & Materials Characterization & Engineering* 3 (2), 65–89.

Hydroxyapatite Based Polymer Composites for Regenerative Medicine Applications

Luis J del Valle and Jordi Puiggali, Chemical Engineering Department, Polytechnic University of Catalonia, Barcelona, Spain

© 2021 Elsevier Inc. All rights reserved.

Introduction

Tissue engineering comprises a set of methods focused to the development of biological substitutes that restore, maintain, or even improve a damaged or diseased tissue (Langer and Vacanti, 1993). Natural, synthetic or semisynthetic materials can be employed to mimic the tissue, being either fully functional or with a capability to grow into the required functionality. Regenerative medicine is considered a broader field that includes tissue engineering as a main topic and is defined as the process of replacing, engineering or regenerating human or animal cells, tissues or organs to restore or establish normal function (Mason and Dunnill, 2008). Selection and design of appropriate materials is one of the main challenges due to the strict number of requirements that should be full accomplished. For example, ideal materials for bone tissue regeneration should mechanically support the damaged area until bone grows in, but in addition should be osteoinductive, osteoconductive, bioresorbable, biocompatible, easy to use, inexpensive and structurally similar to bone (Kwong and Harris, 2008).

Calcium phosphates (CaPs) as well as their composites with both natural and synthetic polymers open a great spectrum of opportunities to render mimicking materials with clearly improved physicochemical, mechanical and biological properties. In addition to their potential use in regenerative medicine, their applications as drug delivery systems have an increasing interest in biomedicine and can in some cases be a complement of its regenerative function. Biodegradable polymers are ideal matrices to form hybrids with CaPs due to have a great design flexibility (e.g., capacity to modify composition and structure). This may allow not only duplicate the characteristics of the extracellular matrix (ECM), but also to accelerate regeneration with respect to natural processes.

Hydroxyapatite (HAp)/polymer composites have a great potential to enhance the healing process of bones, teeth and cartilages (Callister and Rethwisch, 2009). Bones are regenerated, for example, by the action of two differentiated cells lines: osteoblasts, which are mononuclear cells involved in the bone formation process, and osteoclasts, which are multinuclear cells involved in tissue resorption. The natural mineralization process is firstly controlled by cells since nucleation and growth of CaPs take place in their vesicles. Mineral propagation corresponds to the second step that occurs when crystals reach an appropriate dimension. These crystals caused the breakage of the vesicle and become exposed to the collagen and proteins present in the ECM. The mineralization process implies different steps: osteoinduction (i.e., the stimulation of undifferentiated cells to produce osteoblasts and osteocytes), osteoconduction (i.e., the cellular growth into the material, which depends on multiple characteristics like the presence of growth factors and vascularization), and osteointegration (i.e., the contact between the living bone/tissue and the implanted material) (Stevens, 2008). Bone tissue engineering requires to develop complex systems able to provide: Osteogenic cells, a biocompatible scaffold that mimic the ECM, good vascularization to facilitate the efficient transport of both nutrients and wastes, and bioactive signal molecules (e.g. growth factors to promote cell proliferation and morphogens that control tissue generation) (Bharadwaz and Jayasuriya, 2010; Amini *et al.*, 2012).

The present article is organized in several sections that begin with basic topics concerning CaPs and the specific synthesis of HAp. Modification, functionalization and cross-linking of HAp surfaces are then developed. Next steps correspond to the application of HAp as drug delivery systems and non-viral gene carriers. Development of HAp containing hydrogels based on peptide self-assembly and applications in regenerative medicine of scaffolds incorporating HAp are finally explained.

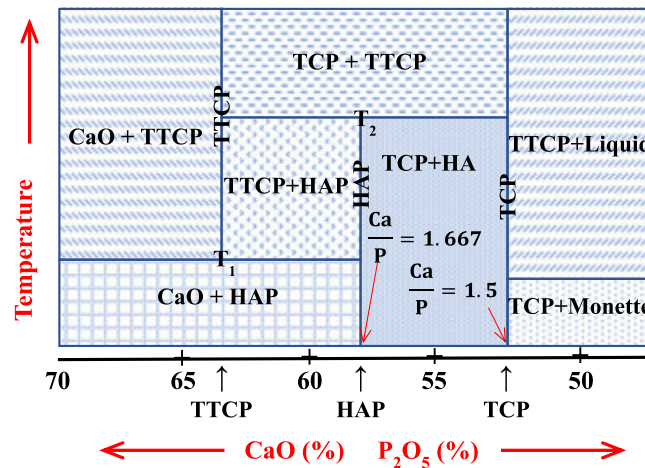
Calcium Phosphates

CaPs have a great interest in different fields (e.g., chemistry, geology, materials science), but probably the most relevant one concerns to biomedical applications due to their wide use as bioceramics, coatings and components in scaffolds for tissue regeneration (Liu and He, 2017; Carino *et al.*, 2018). CaPs can be obtained in different individual phases that differ on their composition, structure, and Ca/P ratio. Degree of substitution (e.g., carbonated substituted compounds), solubility and bioresorbability are also important distinctive features. The most relevant CaPs are brushite (DCPD), monetite (DCPA), octacalcium phosphate (OCP), tetracalcium phosphate (TTCP), tricalcium phosphate (TCP), hydroxyapatite (HAp) and amorphous calcium phosphate (ACP) as indicated in both Table 1 and Fig. 1 (Manjubala *et al.*, 2005). Development of multiphasic systems is currently receiving great attention since none of the above indicated phases gives ideal properties (Dorozhkin, 2016).

OCP is considered the *in vivo* precursor of HAp, which is the thermodynamically stable calcium phosphate form and the main mineral constituent of bone and teeth. Research in bioceramic materials are nowadays mainly focused on TCPs, HAp and biphasic calcium phosphates (BCPs) due to their good biological properties (Kalita *et al.*, 2007). TCPs are characterized by their great degradability and osteoconductivity. Thus, TCPs appear ideal for surgeries involving bone tumors since their dissolution provide a

Table 1 Calcium phosphate phases

Phase	Abbreviation	Compounds	Ca/P ratio
Brushite	DCPD	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	1.0
Monetite	DCPA	CaHPO_4	1.0
Octacalcium Phosphate	OCF	$\text{Ca}_8(\text{PO}_4)_6 \cdot 2.5\text{H}_2\text{O}$	1.33
Whitlockite/Tricalcium Phosphate	TCP	$\text{Ca}_3(\text{PO}_4)_2$	1.5
Calcium Hydroxyapatite	HAp	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	1.67
Tetracalcium phosphate	TTCP	$\text{Ca}_4(\text{PO}_4)_2\text{O}$	2.0
Amorphous Calcium Phosphate	ACP	–	–

**Fig. 1** Equilibrium phase diagram of different phosphate phases. Based on Manjubala, I., Sastry, T.P., Suresh Kumar, R.V., 2005. Bone in-growth induced by biphasic calcium phosphate ceramic in femoral defect of dogs. *Journal of Biomaterials Applied* 19, 341–360.

favorable Ca and P rich environment for bone formation (Ogose *et al.*, 2005). Low pH conditions created by cells that are in direct contact with CaPs make feasible the dissolution process (Peters and Reif, 2004). As previously indicated, HAp is the main mineral component of bones, teeth, cartilages, and calcified tissues. Usually, it occurs as nonstoichiometric sodium, magnesium, and carbonate containing HAp named biological apatite. Manmade HAp can be used as biocompatible and osteoconductive coatings as well as a nanocomponent of scaffolds based on biodegradable polymers. HAp is a good substrate for the adhesion of proteins, peptides, lipids, bacteria, and cell lines (Aronov *et al.*, 2007), enhance biocompatibility of scaffolds and can provide a reinforcing effect in the form of nanoparticles (Ma, 2004; Turon *et al.*, 2017).

The structure of stoichiometric HAp is defined by a monoclinic unit cell, space group $P2_1/b$, with cell parameters of $a = 0.942$ nm, $b = 2a$, $c = 0.688$ nm and $\gamma = 120^\circ$ (Fig. 2). It is interesting to note that OH^- ions are located in two different columns (Kay *et al.*, 1964). All ions point upward in one column, while in the other one point downward. The monoclinic form is obtained only under very strict thermal conditions. At temperatures higher than 250°C there is a structural transition towards a hexagonal unit cell defined by the $P6_3/m$ space group, and parameters of $a = b = 0.943$ nm, and $c = 0.688$ nm (Elliott, 1994). In this case, the mirror symmetry of the space group implies that OH^- ions are statistically disordered pointing upward and downward of the mirror plane. However, some short-range ordering is postulated (e.g., $\text{OH}^-\text{OH}^-\text{OH}^-\dots\text{HO}^-\text{HO}^-\text{HO}^-$). The reversal of the OH^- being favored by the presence of fluorine or chlorine ions and even by a vacancy. Therefore, the hexagonal form is associated to non-stoichiometric compounds (Mathew and Takagi, 2001).

Calcium deficient hydroxyapatite (CDHA) derives from the substitution of calcium and hydroxide ions with protons. In this way CDHA compounds are defined by the formulae $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$ since the interaction of these protons with nearest PO_4^{3-} groups leads to HPO_4^{2-} anions (Dorozhkina and Dorozhkin, 2002). CDHA has higher chemical activity than stoichiometric HAp and plays an important role in bone formation since it induces precipitation of bone-like apatite (Monteiro *et al.*, 2003). Furthermore, this low crystalline CDHA can be slowly resorbed in contrast with the non-resorbable and crystalline HAp. CO_3^{2-} , Mg^{2+} and Sr^{2+} ions can also be easily incorporated in the crystalline structure of HAp by substitution (Bohner, 2000), being logically also enhanced the resorption process.

Synthetic or biological calcium deficient HAp sintered at temperatures higher than 700°C leads to biphasic calcium phosphate (BCP). This is a ceramic material consisting of HAp and TCP that has wide applications for bone grafting. The HAp/TCP ratio depends on the calcium deficiency of the precursor material and specifically decreases when the deficiency increases (Arinzeh *et al.*, 2005).

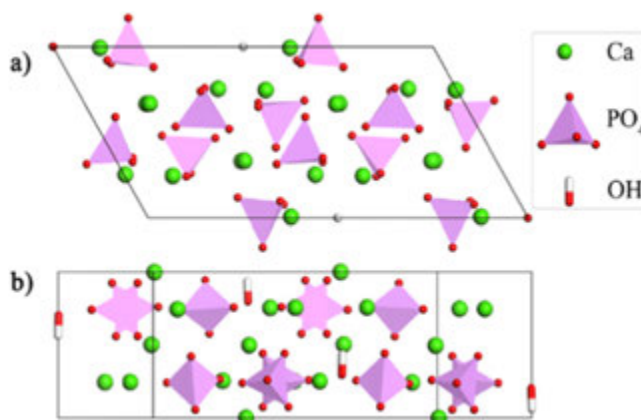
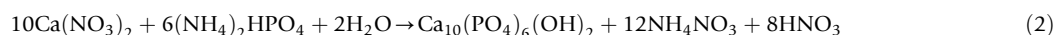
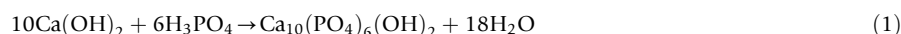


Fig. 2 Structure of the monoclinic form of HAp. (a) View along the *c* crystallographic axis and along a direction perpendicular to the *b* crystallographic axis (b). Reproduced with permission from Ri, M-H., Jang, Y-M., Ri, U-S., *et al.*, 2018. Ab initio investigation of adsorption characteristics of bisphosphonates on hydroxyapatite (001) surface. *Journal of Materials Science* 53, 4252–4261.

Synthesis on Hydroxyapatite

HAp particles are usually obtained through chemical precipitation processes which are mainly based on any of the two following reactions:



The precipitation method is very simple but allows a good control over morphology and particle size by modifying the experimental conditions (Pang and Bao, 2003; Saha *et al.*, 2009; Xia *et al.*, 2009; Ye *et al.*, 2010; Huang *et al.*, 2011). Thus, the pH of the initial solutions can be varied and nanorods, nanowires, microsheets, bur-like microspheres or microflower aggregates be obtained as depicted in Fig. 3 (Zhang *et al.*, 2009). In general, basic conditions lead to an isotropic growth due to the presence of OH^- ions onto the crystal surface, whereas anisotropic crystals are favored at low pH due to the limited amount of adsorbed OH^- ions and the consequent limitation for crystallization and growth of HAp. Fig. 4 shows the influence on the HAp crystal morphology caused by changes on stoichiometry, temperature and pH (Kobayashi *et al.*, 2012).

The addition of chelating agents such as citrates and tartrates (López-Macipe *et al.*, 1998; Ma, 2012) is also a suitable way to control the particle characteristics as well as the use of surfactants (e.g., cetyltrimethylammonium bromide, stearic acid or monosaccharides) (Cao *et al.*, 2004) in the precipitation medium or even the use ethanol as solvent instead of water (Layrolle and Lebugle, 1994). Theoretically HAp should be obtained by mixing the solutions containing the stoichiometric Ca/P ratio (i.e., 1.67), but is frequent that phases with other ratios were also stabilized in the formed crystals depending on the synthetic method and the experimental conditions.

Rapid mixing of solutions containing appropriate amounts of calcium and phosphate ions usually renders an amorphous precipitate (ACP), which can be converted into the crystalline HAp by a subsequent hydrothermal treatment (Ren *et al.*, 2013). This process is highly relevant since allows an accurate control of the final crystal morphology. In addition, self-assembly (Saha *et al.*, 2009; Ye *et al.*, 2010), spray drying (Sun *et al.*, 2009), double emulsion (Shum *et al.*, 2009), solvothermal (Ma and Zhu, 2009) and sol-gel (Dou *et al.*, 2012) methods have been applied to get HAp particles.

Surface Treatment of HAp Nanoparticles

HAp surfaces have a great importance for biomedical applications since they are primordial to establish interactions when implanted with surrounding cells, to absorb and deliver peptides, morphogenetic proteins, antibiotics and drugs (Lee *et al.*, 2014). Absorption of proteins depends for example of the surface roughness (Rechendorff *et al.*, 2006) and charge of the growth face. Ions located on the HAp surface (Ca^{2+} or PO_4^{3-}) can interact with the NH_3^+ and COO^- groups of proteins favouring adsorption.

A precipitation process in presence of amino acids may lead to their immobilization and neutral, acid or basic surfaces depending on the nature of the amino acid. Thus, HAp surfaces having acidic amino acids like aspartic acid are ideal to adsorb positively charged proteins (e.g., lysozyme). For the same reason basic amino acids like arginine can adsorb negatively charged proteins (e.g., serum albumin) (Lee *et al.*, 2012). Incorporation of charged small compounds like citric acid have also been demonstrated efficient for enhancing protein adsorption (Lee *et al.*, 2013b). Surfaces having immobilized arginine-glycine-aspartic acid (RGD) peptides and collagen (COL) are especially interesting since favor cell attachment, cell differentiation and bone remodeling.

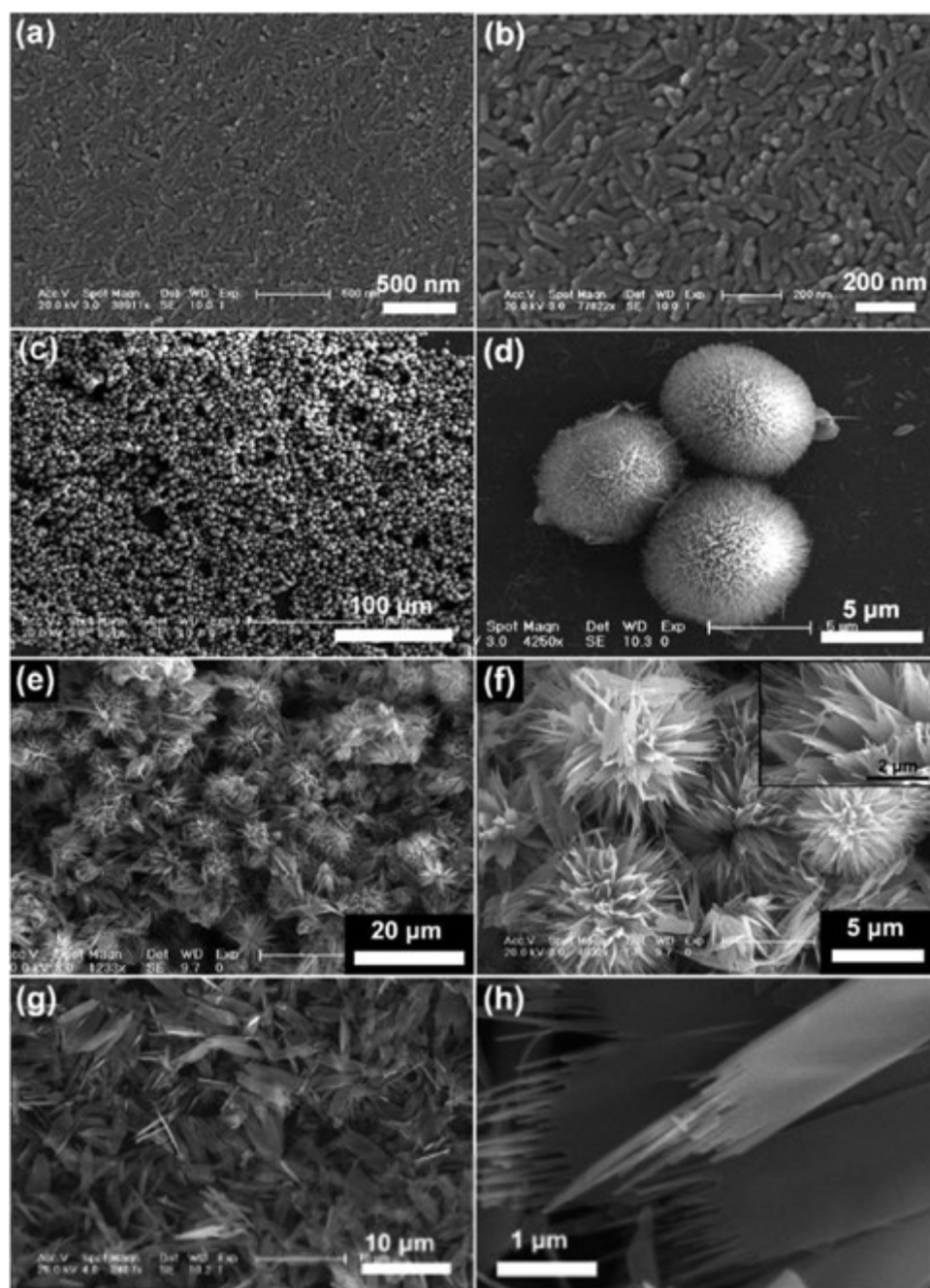


Fig. 3 SEM images showing different morphologies of HAp crystals obtained at different pH values. (a, b) nanorods at pH 7.0, (c,d) bur-like microspheres at pH 5.0, (g, f) microflowers at pH 4.5, and (e, h) microsheets at pH 4.0. Reproduced with permission from Zhang, C., Yang, J., Quan, Z., *et al.*, 2009. Hydroxyapatite nano- and microcrystals with multiform morphologies: Controllable synthesis and luminescence properties. *Crystal Growth & Design* 9, 2725–2733.

A major problem of HAp employed in biomedical applications is the risk of infection caused by the lack of protection from the immune system. Preventive solutions try to avoid the use of antibiotics by the incorporation of Cu^{2+} and Ag^+ ions that are able to inhibit bacterial growth through different mechanisms (Hu *et al.*, 2007; Holt and Bard, 2005; Kim *et al.*, 2007; Lim *et al.*, 2015). Ions can be incorporated by coprecipitation (CP) and ion exchange (IE) (Holt and Bard, 2005). In the first case, the phosphate precursor solution is slowly added over a solution mixture of the calcium precursor and the bactericidal ion, whereas in the second case HAp is immersed in a solution of the bactericidal ion to facilitate ion exchange. The applied methodology affects ion distribution (i.e., bulk or surface for CP and IE, respectively), the bactericide response (fast for IR) and the cytotoxicity (high for IE).

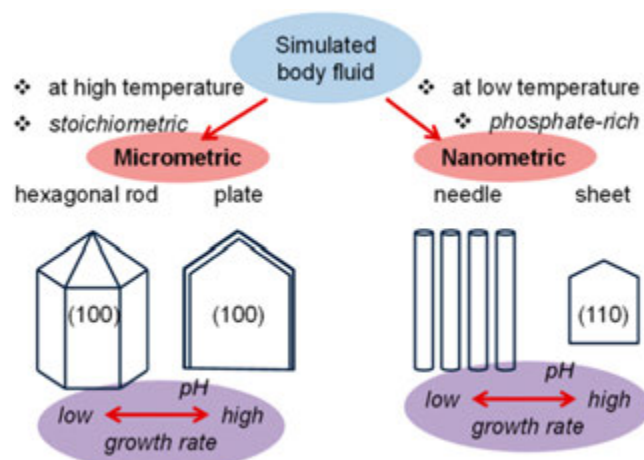


Fig. 4 Influence of the stoichiometric ratio, pH and temperature on the morphology of HAP crystals developed in simulated body fluid (SBF) solutions. Indices indicate the crystal growth faces. Based on Kobayashi, T., Ono, S., Hirakura, S., Oaki, Y., Imai, H., 2012. Morphological variation of hydroxyapatite grown in aqueous solution based on simulated body fluid. *Crystal Engineering Communications* 14, 1143–1149.

Surface modification of HAP can also lead to exfoliated structures that are basic as reinforcing materials (Zuo *et al.*, 2013) and even as carriers for DNA (Zuo *et al.*, 2011). Treatment of HAP with polysaccharides like chitosan (CS) (Zakaria *et al.*, 2013) and even its glucosamine monomer (Luo *et al.*, 2016) has been proved to favor the exfoliation process.

Synthetic bone material substitutes (e.g., BCP) are usually too brittle for long-term applications (Rao, 1995). An interesting strategy to avoid this problem consists on the grafting of an appropriate polymer on the CaP surface. Furthermore, grafting may lead to the improvement of other specific properties such as osteoconductivity (e.g., BCP grafted with poly(glycidyl methacrylate) (Thangavelu *et al.*, 2016)), control of adhesion and cell differentiation by electric stimulation (e.g., HAP grafted with aniline tetramers (Liu *et al.*, 2013)), enhancement of osteoblast proliferation (e.g., HAP grafted with poly(γ -benzyl-L-glutamate) (Wei *et al.*, 2009)). HAP has also been grafted with polylactide (PLA) to improve compatibilization in a nanocomposite having PLA (Hong *et al.*, 2004) or poly(glycolide-co-lactide) (Tang and Liu, 2014) matrices. COL has also successfully grafted onto hydroxyapatite materials following different strategies (Yang *et al.*, 2016; Bhuiyan *et al.*, 2015) that could even render crosslinked materials.

Cross-Linked Materials Derived From Reactions on HAP Surfaces

Poor mechanical properties of hydrogels may limit their inherent applications to regenerate hard tissues systems. Therefore, it appears highly interesting to improve mechanical properties and even to provide functional properties by establishing physical links between the surface of inorganic HAP particles and selected polymers like COL, CS, alginate (ALG) or cellulose.

These biopolymers can be subsequently cross-linked using an appropriate agent as it is the case of genipin (GNP). A typical example corresponds to the reaction of an antiporosis drug (e.g., alendronate, ALN) on the HAP surface and the subsequent formation of a COL-based hydrogel using GNP as an effective crosslinking agent (Fig. 5) (Ma *et al.*, 2016).

Cross-linking of CS with HAP was also possible by reaction of an azide functionalized CS with HAP nanoparticles incorporating alkyl groups (Pradal *et al.*, 2011). These particles were prepared by the addition of propiolic acid in the typical precipitation medium employed for HAP synthesis (Wei *et al.*, 2014). Dopamine was also employed as a cross-linker agent between HAP and CS, having the derived materials improved mechanical performance and cell adhesion (Prajatelistia *et al.*, 2015).

Incorporation of HAP into a polymer matrix may promote a gelling process due to the release of Ca^{2+} ions that could establish interactions with, for example, the carboxylic groups of different biopolymers. It is interesting to note that inorganic nanoparticles can also provide a clear reinforcing effect of the matrix. Thus, HAP was appropriate to promote the gelation of the anionic pectin polysaccharide giving rise to an injectable system for bone tissue regeneration (Munarin *et al.*, 2015).

Partial release of Ca^{2+} ions from HAP was also fundamental to establish cross-linked hydrogels with ALG and CS (Sukhodub *et al.*, 2016). Hydrogels were formed in the precipitation stage by means also of interactions between hydroxyl, amino and carboxyl groups of the indicated biopolymers.

Three-dimensional nanocomposite structures have been developed by in situ synthesis of HAP in presence of carboxymethyl cellulose through physical cross-links between Ca^{2+} ions and carboxyl groups (Garai and Sinha, 2014). This process mimics bone formation due to the simultaneous occurrence of synthesis and assembling in the organic matrix and lead to materials with high compressive stress, high modulus and applicability as bioactive bone grafting.

Cross-linked systems can also be produced by using synthetic polymers like polycaprolactone diacrylate. In this case, HAP was added before to initiate a thermal cross-linking process that led to porous materials with high modulus and osteoconductivity (Koupaei and Karkhaneh, 2016).

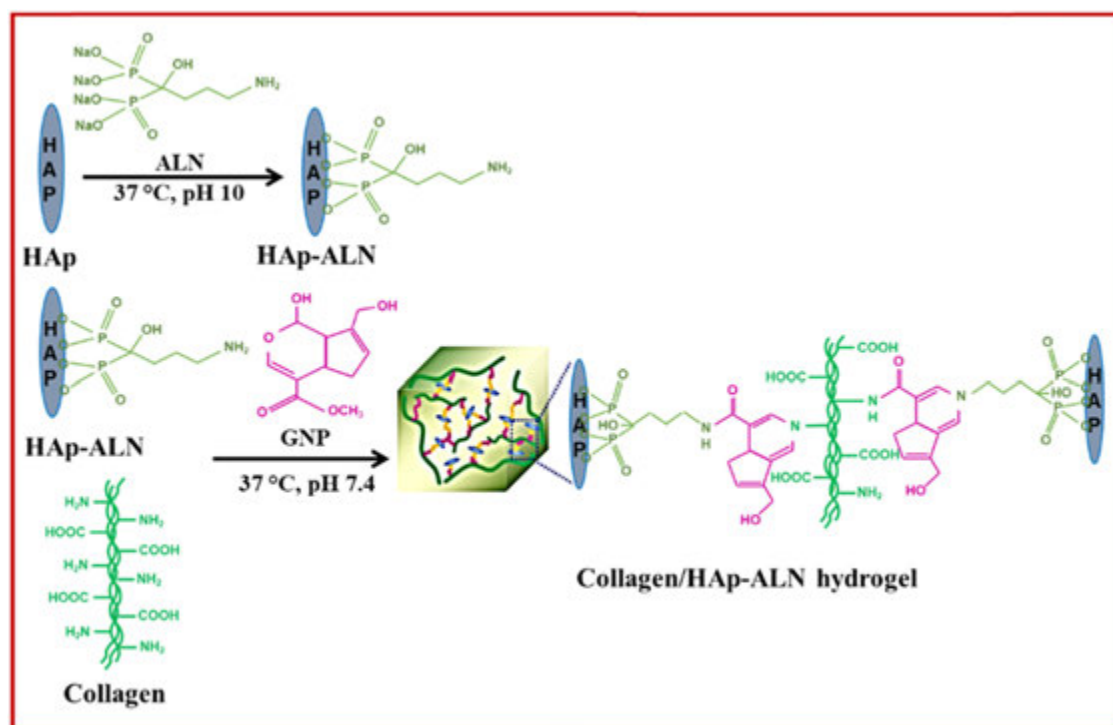


Fig. 5 Synthesis of COL/HAp-ALN hydrogels. Based on Ma, X., He, Z., Han, F., *et al.*, 2016. Preparation of collagen/hydroxyapatite/alendronate hybrid hydrogels as potential scaffolds for bone regeneration. *Colloids and Surfaces B: Biointerfaces* 143, 81–87.

Applications of HAp Based Materials as Drug Delivery Systems

The high adsorption and binding capability of HAp surfaces has been explained in the previous sections and appears a fundamental property to develop drug delivery systems. Furthermore, HAp can be dissolved in acidic environments as the lysosome vesicles of cells and even in the acidic extracellular environment of cancer cells. Therefore, both bulk incorporated compounds during the synthesis procedure and surface adsorbed bioactive molecules can efficiently be released. In the first case, a homogeneous distribution and a slow release can be attained, while in the second case a local, scarcely controllable and fast delivery are characteristic. Obviously, the control on the nanoparticle morphology (e.g., needle- plate-shaped or spherical) are primordial to tailor a specific therapeutic behavior (Roveri and Iafisco, 2010).

Antibiotics and growth factors and typical drugs that improve the performance of materials employed in tissue regeneration since they can prevent infections and promote osteoblast differentiation. A sustained work has been performed to develop systems with a local and controlled delivery of encapsulated bone morphogenetic proteins in order to protect bioactivity and prolong their beneficial effect (Liu *et al.*, 2009). Thus, HAp/COL-ALG bionanocomposites loaded with morphogenetic proteins have been successfully developed as a bone filler (Sotome *et al.*, 2004). In a similar way, fibroblast growth factors have been incorporated in HAp/COL bionanocomposites leading to efficient materials to promote bone and cartilage regeneration (Maehara *et al.*, 2010). The (PDGF)-BB grown factor has also been adsorbed in the HAp surface of polycaprolactone (PCL) /COL/HAp nanocomposites, giving rise to an enhanced stimulation of osteoblast chemotactic migration and therefore favouring the bone healing process (Phipps *et al.*, 2012).

As indicated in the previous section ALN is a bisphosphonate with a great capability to suppress bone resorption. Therefore, HAp nanoparticles carrying this drug are interesting since allow combining the osteoconductive properties of HAp with a well-recognized therapeutic effect against osteoporosis. Highly promising results have been achieved using spherical HAp nanoparticles coated with successive layers of poly(allylamine) and ALG, which makes feasible the ALN conjugation (Hwang *et al.*, 2016).

Incorporation of minocycline, a tetracycline antibiotic, has been evaluated due to additional advantages related to the enhancement of bone formation and the decrease of bone resorption. A slow release, and improvement of cell adhesion, proliferation and differentiation was demonstrated for HAp-gelatin nanocomposites loaded with minocycline (Dou *et al.*, 2011). Doxycycline and dexamethasone have also been incorporated in complex systems based on COL and having HAp rods to prevent infection and increase osseointegration (Song *et al.*, 2013a). Different studies have been focused in the load and release of gentamicin due to the positive effect of this aminoglycoside antibiotic against the osteomyelitis disease (Shi *et al.*, 2010; McNally *et al.*, 2016). ALG/HAp nanocomposites loaded with erythromycin provided an antibiotic effect, showed high osteoconduction and resorbability, and had a potential use as an injectable bone filling material (Ferraz *et al.*, 2007).

CDHA/CS nanocomposites loaded with vitamins have also been developed. Nanocrystals were fundamental as effective bioactive fillers and as regulators of the delivery process (Liu *et al.*, 2006).

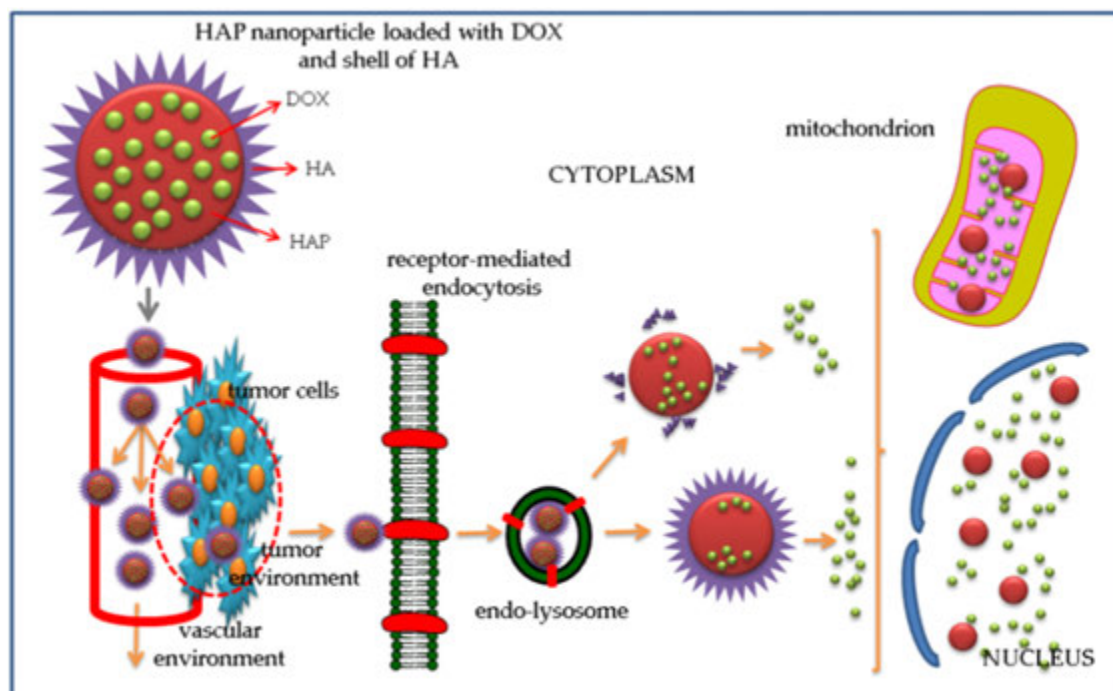


Fig. 6 Targeted antitumor drug delivery mechanism (nucleus and mitochondrion) of HAP-HAP nanoparticles loaded with DOX. Based on Xiong, H., Du, S., Ni, J., Zhou, J., Yao, J., 2016. Mitochondria and nuclei dual-targeted heterogeneous hydroxyapatite nanoparticles for enhancing therapeutic efficacy of doxorubicin. *Biomaterials* 94, 70–83.

Ca^{2+} ions of HAP can lead to an antiproliferative cancer cell activity and the stimulation of intracellular apoptotic signals (i.e., the activation of caspase protein digesting enzymes and the release of cytochrome C from mitochondria) (Liu *et al.*, 2003; Tang *et al.*, 2014). Therefore, HAP nanocapsules appear as an ideal encapsulation medium of anticancer drugs taking advantage of their inherent activity. The efficacy of the apoptosis effect of HAP seems to increase when the size of nanoparticles decreased (Yuan *et al.*, 2010; Li *et al.*, 2008), a feature that suggests a correlation with cellular internalization (Cui *et al.*, 2016).

Cancer tissues are characterized by an enhanced permeability and retention (EPR), which can be in some cases considered for selective targeting by nanoparticles. The potential control of size and morphology (e.g., spheres, rods or needle-like crystals), and the easy way to perform surface modifications appear a great advantage of employing HAP as drug carrying nanoparticles for cancer treatment. Thus, particles loaded with positively charged CS can establish good interactions with negatively charged cancer cell membranes (Yang and Hon, 2009). This approximation has been for example employed for the treatment of colon cancer by encapsulating celecoxib in this coated system (Venkatesan *et al.*, 2011).

HAP nanoparticles coated with hydrophilic hyaluronic acid (HA) have also been loaded with anticancer drugs as doxorubicin and revealed a promising potential against tumor cells. In fact, HAP facilitates a targeted cancer therapy due to its affinity with glycoproteins that are overexpressed in tumor cells (Fig. 6) (Xiong *et al.*, 2016).

Chloramphenicol (CAM) is a wide-spectrum antibiotic that can induce mitochondrial-dysfunctions in cancer cells. This property has been considered for developing new platforms for cancer therapy. Thus, CAM has been encapsulated in both HAP and ACP nanoparticles coated with pyrophosphates in order to protect the antibiotic during and/or after its release. The greater therapeutic efficacy was found when amorphous particles and a triphosphate coating were employed (Rivas *et al.*, 2018). CAM distribution in the nanoparticles can be varied depending on the precipitation method (Rivas *et al.*, 2019b). In this way, a preferred distribution on the outer part of the particle could be attained giving rise to a fast bactericide effect.

HAP as a Gene Carrier

Immunotherapy strategies allow to boost the immune system of a patient to kill cancer cells or act against other acquired or inherited diseases. The development of non-viral gene carriers is gaining attention since can transport specific disease-associated antigens (Palena *et al.*, 2006). Therefore, the use for example of more conventional surgery, chemotherapy and radiotherapy alternatives can be avoided for the cancer treatment.

Non-viral gene vectors have advantages derived from a scarce (and even null) immunogenicity, easy sample preparation, low cost, and high flexibility to locate selected transgenes with different sizes (Santos *et al.*, 2011). HAP has most of these advantages

and furthermore can establish good interactions with DNA, being an ideal transfection and protection medium. HAp-DNA complexes can be obtained by different methods such as coprecipitation (Bisht *et al.*, 2005), encapsulation (Sokolova *et al.*, 2006) and coating (Welzel *et al.*, 2004). Fig. 7 shows the preparation of nanoparticles with sizes around 100 nm (i.e., appropriated to be endocytized by cells) by coprecipitation in the aqueous core of micellar entities. Modifications of particles is usually necessary in order to prevent their aggregation (e.g., coating with CS (Lee *et al.*, 2013a)), to increase the loading efficiency (ionic substitution with magnesium or strontium for calcium and carbonate or fluorine for phosphate anions) and even to facilitate the dissolution after endocytosis (Chowdhury *et al.*, 2004; Chowdhury, 2011; Hanifi *et al.*, 2010).

Dynamic simulations demonstrated the capability of HAp to encapsulate the double helix of DNA without causing a significant distortion of its secondary structure (Fig. 8) (Revilla-López *et al.*, 2013). Ionic interactions between calcium ions of HAp and the phosphate groups of DNA were essential to form complexes able to act as nucleating agents. These theoretical considerations were experimentally verified (TEM, UV, XPS and electrophoretic techniques) since DNA was encapsulated in both HAp and ACP forms (Manjubala *et al.*, 2005).

Multiple works have been performed about the use of HAp nanoparticles as gene carrier vectors. Thus, structured HAp was found to be able to protect DNA from DNase digestion/degradation (Zuo *et al.*, 2011), pDNA adsorbed on HAp nanocrystals was efficiently transfected into cancer SGC-7901 cells (Zhu *et al.*, 2004), HAp encapsulating malarial merozoite protein-119 showed promising properties to be employed as antigen carriers for immunopotentialization (Goyal *et al.*, 2009), complexes of HAp with arginine have been successfully employed for the treatment of nasopharyngeal carcinoma cells (Chen *et al.*, 2010b), new therapeutic matrices for bone repair have been developed by incorporating the ephrinB2 gene in HAp nanoparticles embedded in a COL matrix (Tierney *et al.*, 2013).

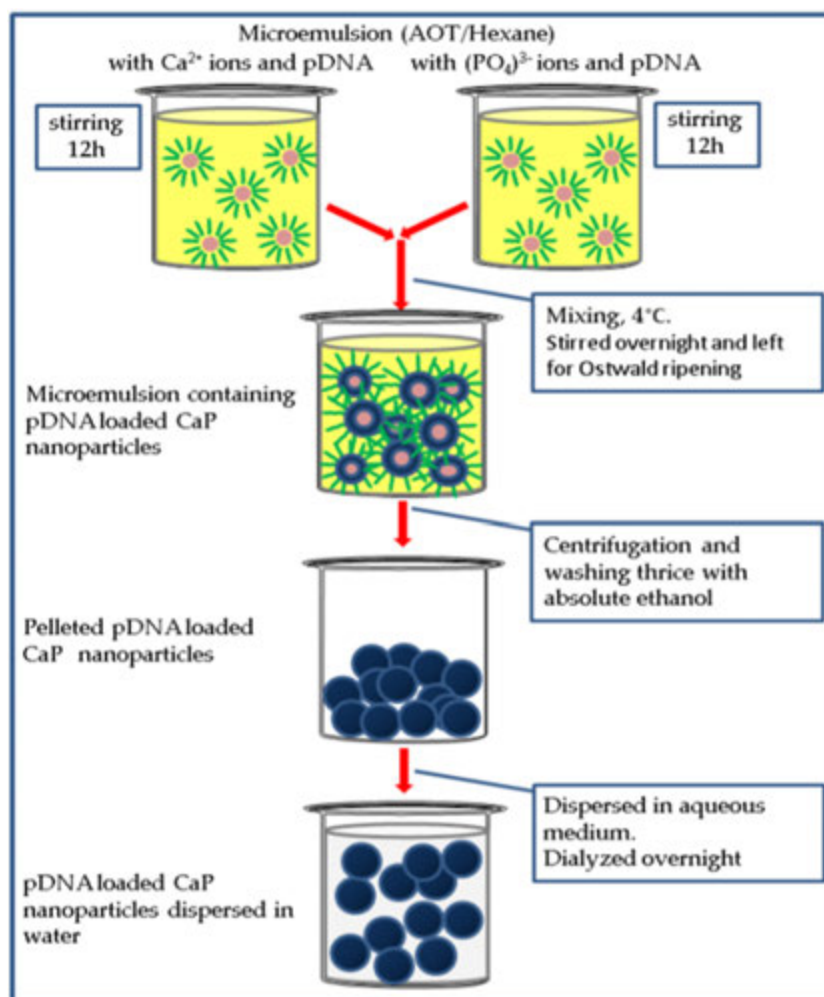


Fig. 7 Scheme showing the encapsulation of plasmid DNA (pDNA) by the coprecipitation method and using a bis(2-ethylhexyl) sulfosuccinate surfactant (AOT) microemulsion in hexane. Based on Bisht, S., Bhakta, G., Mitra, S., Maitra, A., 2005. pDNA loaded calcium phosphate nanoparticles: Highly efficient non-viral vector for gene delivery. *International Journal of Pharmaceutics* 288, 157–168.

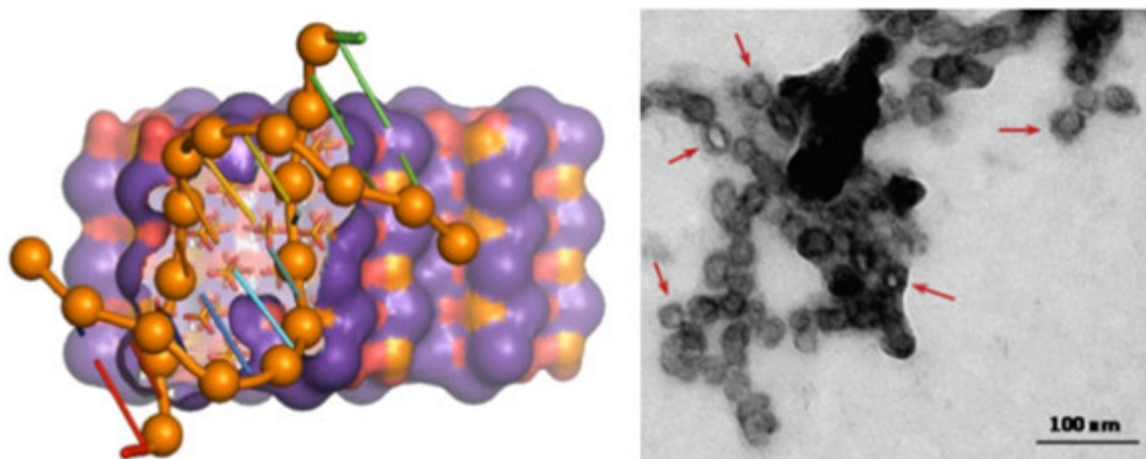


Fig. 8 Simulated HAp structure obtained using DNA as a nucleating agent(left). TEM micrographs showing HAp-DNA nanocapsules (right). Capsules with a clearly distinctive contrast that suggest the incorporation of DNA are indicated by red arrows. Reproduced with permission from Revilla-López, G., Casanovas, J., Bertran, O., *et al.*, 2013. Modeling biominerals formed by apatites and DNA. *Biointerphases* 8, 10. Bertran, O., del Valle, L.J., Revilla-López, G., *et al.*, 2014. Mineralization of DNA into nanoparticles of hydroxyapatite. *Dalton Transactions* 2014, 43, 317–327.

Peptide/HAp Based Hydrogels for Biomedical Applications

Peptide molecules have a self-assembly ability that has been considered for the development of new hydrogels (Hartgerink *et al.*, 2002; Stupp, 2005). These can mimic the extracellular matrix and have been proved very appropriate for different biomedical applications (e.g., regeneration of hard tissues) (Rivas *et al.*, 2019a). Peptide-based hydrogels show inherent advantages like biocompatibility, capacity to establish physical and reversible cross-links under physiological conditions, and trigger capacity. Furthermore, materials can be designed with a great tunability taking advantage of varying amino acid sequence and peptide length, which influence on the final structure and functionality.

The great potential of such materials is obviously linked to the great variability in the composition and length of peptides, which opens the possibility of a tailored design to suit a specific property. The incorporation of charged amino acids in the peptide sequence promotes the interaction with calcium divalent ions, making it possible to use the derived hydrogels for the nucleation of HAp and even the development of nanocomposites. Promising results have been achieved in recent years concerning the development of hydrogels for the regeneration of hard tissues, mainly bone, teeth, and cartilage, as evidenced in the present review.

Peptides can self-assemble following different mechanisms that lead to typical β -sheet structures: (1) Ionic interactions between complementary peptides having opposite charges (positive and negative charges provided by hydrophilic residues like lysine/arginine or aspartic/glutamic, respectively) (Raspa *et al.*, 2014); (2) RADA sequences characterized by an alternate disposition of hydrophilic and hydrophobic units (e.g., Arg-Ala-Asp-Ala sequence with positive and negative arginine and aspartic hydrophilic residues and alanine as hydrophobic residue) (Hori *et al.*, 2007); (3) L,D-heterochiral peptides (Fuertes *et al.*, 2017); Peptide amphiphiles (Hartgerink *et al.*, 2001), and (4) Peptides with N-protected groups able or establish interactions (Tao *et al.*, 2016).

New bionanocomposites based on peptide self-assembling and HAp nanoparticles are characterized by a hybrid structure having inorganic (HAp) and organic (peptides) components that mimics the ECM. Preferred particles have a high aspect ratio and diameters in the nanoscale range. Self-assembling peptides (SAP) constituted an appropriate environment for the cell growth and were able to enhance both cell adhesion (e.g., bone marrow mesenchymal stem cells (BMSCs)) and osteoblast differentiation (Botchwey *et al.*, 2003; Zhang *et al.*, 2018). These characteristics are meaningful in hard tissue regeneration since one of its major problems concern the limited number of cells that can be loaded in the designed scaffolds (Mankani *et al.*, 2011). SAP/nHAp/CHI scaffolds have been, for example, employed to repair femoral bone defects. Non-acidic SAPs (e.g., the SPG-178 peptide based on arginine, alanine, leucine and aspartic acid) were successfully employed together with human bone morphogenetic protein, being detected a clear enhancement of cell proliferation, osteogenic differentiation, and COL and osteocalcin expression (Tsukamoto *et al.*, 2017).

(LE)₈ and (VEVSVKVS)₂ peptides were able to self-assemble, giving rise to nanofibers that could form hydrogels through ionic cross-linking between the carboxyl groups of glutamic acid and added calcium ions. The system was ideal as bone-filling material and could mineralize both HAp and ACP along nanofibers under neutral and basic pHs (Nonoyama *et al.*, 2012).

The external coating of teeth is constituted by an anisotropic arrangement of HAp crystals that is named enamel (Paine *et al.*, 2001). This arrangement is regulated by amelogenin, a protein that is finally eliminated by the action of proteolytic enzymes (Fukumoto *et al.*, 2004). Large enamel lesions are difficult to be repaired, being nowadays interesting the use of self-assembled scaffolds to control HAp growth and provide a mimetic enamel structure (Elkassas and Arafa, 2017). In this way, the peptide amphiphile having a high content of the epitope RGDS was found suitable to induce growth of HAp according to the native

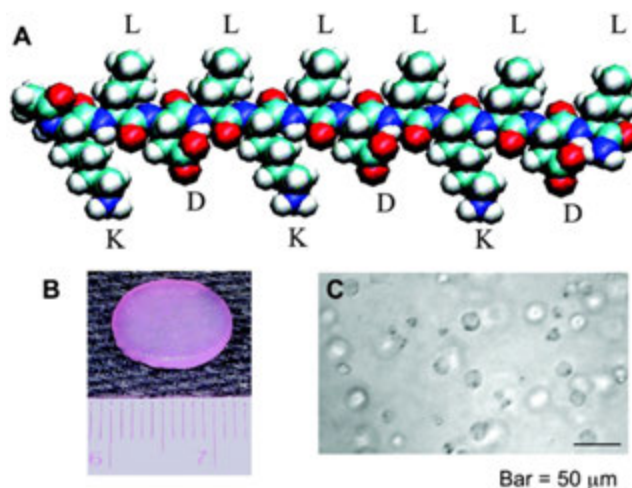


Fig. 9 (A) Molecular model of a KLD-12 self-assembling peptide based on alternating hydrophobic (leucine, L) and hydrophilic (positively and negatively charged lysine, K, and aspartic acid, D) residues that facilitates self-assembling through intermolecular interactions. (B) A 12-mm chondrocyte-seeded peptide hydrogel plug. (C) Light microscope image of chondrocytes encapsulated in peptide hydrogel. Reproduced with permission from Kisiday, J., Jin, M., Kurz, B., *et al.*, 2002. Self-assembling peptide hydrogel fosters chondrocyte extracellular matrix production and cell division: Implications for cartilage tissue repair. *Proceedings of the National Academy of Sciences of the United States of America* 99, 9996–10001.

enamel structure (Huang *et al.*, 2010). Another interesting example is the Ac-Gln-Gln-Arg-Phe-Glu-Trp-Glu-Phe-Glu-Gln-Gln-NH₂ peptide that is able to self-assemble under the low pH of a caries lesion and act as nucleation agent for HAp (Alkilzy *et al.*, 2018). Self-assembly of Fmoc-Val-cetylamine led to nanofibrous gels with great affinity towards HAp and ability to mimic the ECM of osteoblasts (Romanelli *et al.*, 2015).

The cartilaginous matrix mainly consists of COL and proteoglycans, and is produced and maintained by chondrocyte cells. Osteoarthritis is a typical cartilage disease that leads to the loss of functionality and mechanical properties as consequence of the depletion of glycosaminoglycans (Katta *et al.*, 2008). Regeneration of cartilages is hardly difficult due to their avascular character and the absence of stem cells. Strategies for the repair of cartilages are mainly based on the implantation of mesenchymal stem cells (MSCs). Thus, injectable therapies have been feasible by seeding MSCs into AcN-(KLDL)₃-CNH₂, a self-assembled peptide hydrogel able to support the chondrogenesis of the encapsulated cells (Kisiday *et al.*, 2018). Other interesting approaches consist on the use of: (1) Osteochondral constructs based on the HAp interdigitation with a self-assembled neocartilage constituted by COL and glycosaminoglycan (Brown *et al.*, 2018), (2) SAP hydrogels able to retain chondrocytes and facilitate the achievement of a cartilage ECM (Fig. 9) (Kisiday *et al.*, 2002). SAPs based on tryptophan, phenylalanine and charged amino acids (Barco *et al.*, 2018) are interesting since can be delivered as no-viscous fluids that self-assemble once placed in the damaged tissue.

HAp Based Scaffolds for Tissue Regeneration

Scaffolds appropriate for tissue regeneration should have a porous structure, playing the control of geometry, pore size and pore interconnectivity a fundamental role. Different methodologies have been developed to prepare these porous scaffolds, being probably phase separation and electrospinning the most significant techniques.

Thermally induced phase separation (TIPS) gives rise to polymer lean and rich phases by cooling a homogeneous polymer solution. A porous solid structure is derived from the rich phase after solvent removal. Different morphologies (e.g., open or close pores, membrane or fibrous structures) can be attained depending on the separation conditions (e.g., polymer concentration and molecular weight, cooling path) (He *et al.*, 2009). In addition, water soluble porogens can also been added to the initial solution. PLA/HAp scaffolds have been for example prepared by TIPS to mimic the bone matrix and the nanofeatures of bone (Zhang and Ma, 1999).

Polymer fibers with similar dimension than the fibrils existing in the ECM can be obtained by means of the electrospinning technique (Doshi and Reneker, 1995). This is based on the application of a high voltage to polymer solution drops. A charged jet is formed when the applied electrostatic charge is able to overcome the surface tension of solution drops slowly ejected through a capillary. The polymer jet is subsequently deposited into a grounded collector in the form of accumulated micro/nanofibers. Characteristics of scaffolds can be modified according to solution properties (e.g., solvent, polymer concentration and viscosity), environmental conditions (e.g., temperature and humidity) and processing parameters (e.g., applied voltage, flow rate and tip-collector distance).

Electrospinning has some inherent problems that corresponds to the use of solvents since they may be prejudicial for some natural polymers susceptible of denaturation (e.g., the triple helix structure of COL may be lost giving rise to gelatine

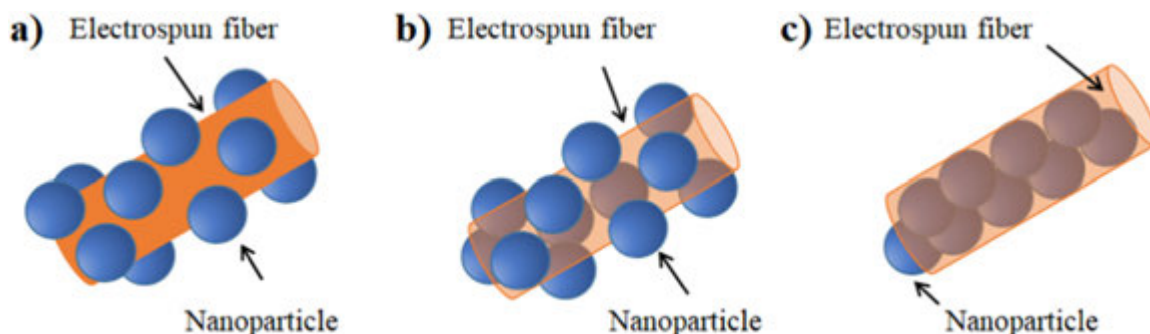


Fig. 10 Incorporation of nanoparticles into electrospun fibers: (a) Surface attachment, (b) Partial encapsulation and (c) Complete encapsulation. Based on Tong, H.W., Wang, M., Li, Z.Y., Lu, W.W., 2010. Electrospinning, characterization and in vitro biological evaluation of nano-composite fibers containing carbonated hydroxyapatite nanoparticles. *Biomedical Materials* 5, 054111.

(Zeugolis *et al.*, 2008)), and even they can be retained in the electrospun fiber causing some cytotoxicity. In addition, homogenization of the initial solution may be difficult due to its usual high viscosity.

HAp particles can be easily incorporated in the electrospun fibers by dispersing them in the initial polymer solution (i.e., before processing). Depending on the ratio between the dimension of particles and the diameter of fibers, different distributions can be attained. Surface attachment, partial encapsulation and complete encapsulation are derived when the diameter is lower, similar or greater than the particle size (Fig. 10).

The complete encapsulation should lead to materials with higher mechanical performance, while surface attachment appears ideal to enhance the bioactivity (Tong *et al.*, 2010). Usually, the incorporation of HAp particles reduces the homogeneity and regularity of the electrospun fiber and increase the thickness. The optimization of processing parameters may improve the homogeneity and even diminish the formation of clumps.

Encapsulation of HAp inside fibers may decrease the expected bioactivity provided by the isolated nanoparticles (He *et al.*, 2014), the effect being more significant as the porosity of the scaffold decreases. Mineralization of the scaffold surface (e.g., by a subsequent electrodeposition process) is an interesting solution to keep biological activity.

Scaffolds incorporating HAp for tissue engineering applications are based on natural, modified natural and synthetic polymers. In the first group, COL/gelatin, silk fibroin (SF), ALG and CS are the most relevant. Cellulose acetate is a clear example of the second group, while PLA, PLGA, PCL, poly(hydroxybutyrate) (P3HB), polyvinyl alcohol (PVA) and polyethylene glycol (PEG) are the most employed polymers of the third group. Obviously, mixtures of polymers belonging to different groups have also been employed. Natural polymers seems better than synthetic ones in terms of biocompatibility, degradation rate and lower toxicity of degradation products (e.g., it can be avoided the typical release of acid compounds in the surrounding tissue from PLGA and PLGA polyester matrices), but synthetic polymers offer great possibilities to get enhanced properties through the control of composition and even of the surface topography.

ALG is probably the most applied natural polymer for regeneration of bones, cartilages and even skin due to a similar chemical structure to glycosaminoglycan, which is a major component of the ECM. Carboxylic groups of ALG can form ionic interactions with calcium cations (Zheng, 1997), being these linkage sites able to nucleate and facilitate the growth of HAp crystals in electrospun ALG fibers impregnated with PO_4^{3-} ions (Fig. 11). Resulting scaffolds showed low agglomeration of HAp nanoparticles and high attachment of osteoblasts (Chae *et al.*, 2013).

CS has also a great application due to a skeleton highly similar with glycosaminoglycans and the presence of hydroxyl and amine groups that makes feasible and easy chemical modification. Probably, CS/HAp scaffolds have mostly been prepared by the freeze-drying technique, being demonstrated the reinforcing effect of HAp nanoparticles (e.g. incorporation of 20 wt% of HAp increased the modulus from 3.0 to 4.4 GPa) (Nazeer *et al.*, 2017; Pighinelli and Kucharska, 2013).

COL is the main organic component of the ECM of hard tissues and logically displays good biocompatibility and facilitates cell adhesion and proliferation. Nevertheless, scaffolds based only in COL have a limited interest for bone tissue regeneration due to a very fast degradability, poor mechanical properties and high swelling ratio. Therefore, scaffolds with HAp are receiving increasing attention (Zhou *et al.*, 2016). COL/HAp scaffolds have been revealed highly interesting for the treatment of periodontitis bone imperfections (Liu *et al.*, 2016). The high regeneration capability was demonstrated through both good deposition of new bone structures and vascularization at the imperfection sites, which could be caused by an appropriate interaction between organic and inorganic phases. Porous COL scaffolds incorporating BCP nanoparticles and dexamethasone (DEX) have been prepared by the porogen leaching method (Chen *et al.*, 2018). Materials showed a high osteogenic differentiation of MSCs, which was attributed to the constant release of calcium, phosphate and DEX ions, high biocompatibility and angiogenesis effect.

Electrospun cellulose/HAp nanofibers have been found appropriate to prepare new scaffolds for bone tissue regeneration (Ao *et al.*, 2017), being the size distribution of nanofibers similar to the natural ECM fibers of natural bone. Mechanical properties of the derived scaffolds could reach modulus of elasticity and tensile strength values around 3 and 70 GPa, respectively.

The hydrophobic nature of some synthetic polymers (e.g., PLA, PLGA, PHB and PCL) favors the aggregation of the inorganic HAp particles and enhances the indicated irregular morphology of the electrospun fibers with a high presence of beads. To

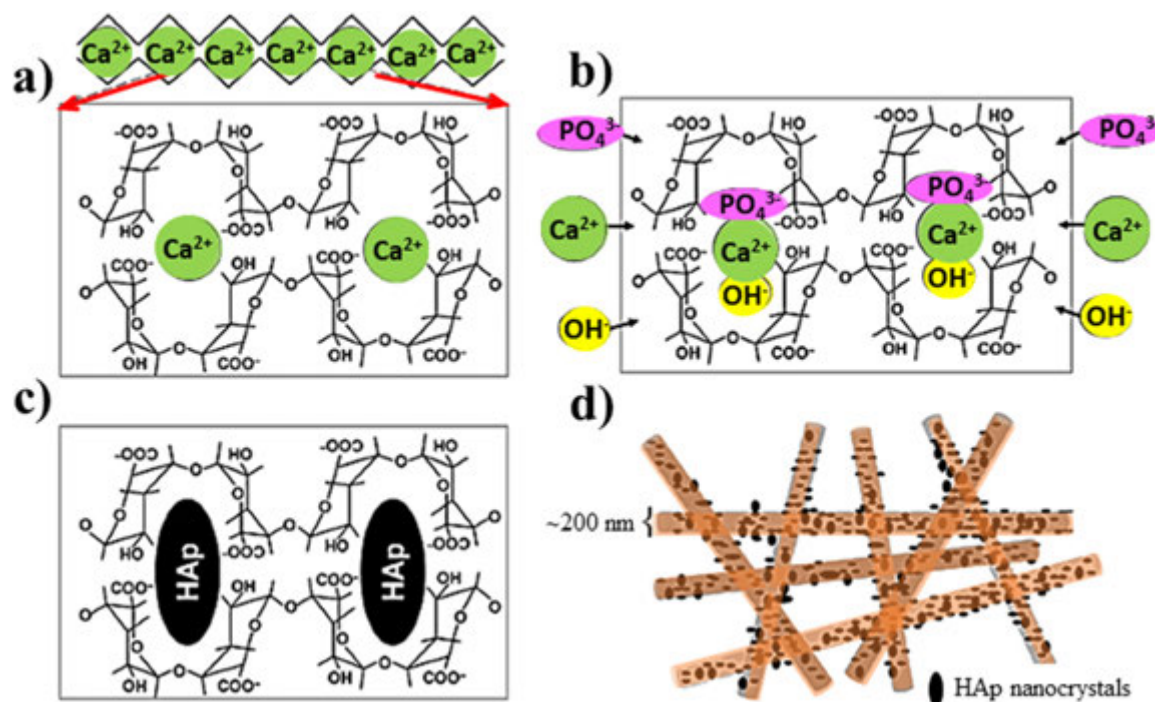


Fig. 11 (a) Scheme showing the structure of the “egg box” model of calcium ALG. (b) Calcium ALG incorporating precursor ions for HAp nucleation. (c) mineralized “egg-box” structure with HAp. (d) Scheme showing the cross-linked/in situ synthesized HAp/ALG nanocomposite fibrous scaffold. Based on Chae, T., Yang, H., Leung, V., Ko, F., Troczynski, T., 2013. Novel biomimetic hydroxyapatite/alginate nanocomposite fibrous scaffolds for bone tissue regeneration. *Journal of Materials Science: Materials in Medicine* 24, 1885–1894.

minimize this effect, surfactant molecules can be added to stabilize the HAp/polymer interphase (Kim *et al.*, 2006). Compatibility between the selected polymer and HAp is an additional problem that has in some cases solved by grafting appropriate molecules on the surface of HAp particles. For example, ring opening polymerization of lactide has been performed in the presence of HAp, PLA oligomers were successively grafted to particles having hydroxyl functionality (Song *et al.*, 2013b). HAp can establish good interactions with hydrophilic polymers like PEG so it is a good candidate for developing new scaffolds. Unfortunately, PEG has severe limitations since it is not degradable and furthermore its processing into electrospun nanofibers is difficult. The use of block copolymers (e.g., polylactide-polyethylene glycol-polylactide, PELA) has been undertaken with promising results concerning enhancement of osteochondral cell growth and osteogenic cell expression (Weiner and Wagner, 1998). PEG is also an interesting blending component since its high hydrophilicity facilitates water access in the polymeric matrix and enhanced the degradation of other components like gelatin (Zhou *et al.*, 2016) or SF (Qui *et al.*, 2019). The case of SF is relevant since HAp facilitates the osteogenic differentiation of MSCs and improves mechanical properties, but delays the degradation of SF. Therefore, the blending with PEG can effectively produce a counterbalance effect.

Electrospun PLA scaffolds have also been grafted on their surface with CS through its amine functional groups. HAp can subsequently be deposited on the membrane surface after immersion in simulated body fluid (SBF) (Thien *et al.*, 2013) in a similar way as performed with CS nanofibers (Chen *et al.*, 2013a). In both cases, cell viability was increased after a HAp growth that was facilitated by hydroxyl and amine groups of CS. The mineralization process was effective in a maximum incubation period of six days. In the case, of the PLA/CS scaffold the degradation rate was clearly enhanced with respect to that obtained from pure and hydrophobic PLA.

Poly(vinyl alcohol) (PVA) is another hydrophilic polymer that has interests as a scaffold component. PVA is one of the very few vinyl polymers that is susceptible to degradation under both aerobic and anaerobic conditions (Halima, 2016). Furthermore PVA has good mechanical properties, has an anabolic effect on bone formation, and can be cross-linked through its multiple hydroxyl groups (Sailaja *et al.*, 2009). Electrospun fibers constituted by COL, PVA and HAp have been reported, showing the derived scaffolds good adhesion and proliferation of bone cells (Song *et al.*, 2012). PVA electrospun fibers have also been mineralized by incubation in solutions containing calcium and phosphate ions. Porous scaffolds for tissue engineering applications were derived (Chang *et al.*, 2013). Electrospun coaxial nanofibers having PLA (shell) and PVA (core) have also been prepared (Alharbi *et al.*, 2018). Scaffolds showed appropriate biocompatibility, enhanced mechanical properties (i.e., ductility increased from 40% for pure PLA nanofibers to 110%) and high hydrophilicity (i.e., the water contact angle was so low as 25°). Basically, the water molecules could pass through the PLA channels/porous and be absorbed in the hydrophilic PVA core.

Incorporation of HAp particles on polyester matrices is beneficial since could slow down their degradation rate in HAp-dependent manner but more interestingly basic HAp can neutralize the acidic byproducts generated during the polymer degradation process causing a lower inflammatory response after the scaffold implantation.

PCL is an interesting synthetic polymer due to its appropriate biocompatibility, and high toughness and mechanical strength, (Shor *et al.*, 2007). Probably, the slow degradation rate of PCL and its high hydrophobicity may hamper potential applications in tissue engineering (Fabbri *et al.*, 2010). Nevertheless, PCL scaffolds containing HAp showed promising biological characteristics. Thus, the *in vivo* bone generation efficiency of electrospun PCL/HAp scaffolds has been demonstrated (Fu *et al.*, 2012). Surface modification of PCL scaffolds has been performed by electrospraying HAp. Specifically, adhesion, proliferation and differentiation of MSCs was demonstrated, being this treatment available for other polymeric matrices (Venugopal *et al.*, 2013). Complex bioinspired honeycomb systems based on electrospun PCL fibers and electrosprayed HAp particles were obtained using a micropatterned collector. These scaffolds showed a great potential in maxillofacial surgery (Naudot *et al.*, 2020).

Electrospinning has also been combined with electrodeposition techniques in order to produce mineralized scaffolds. Aqueous electrolytes containing, for example, $\text{Ca}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ can be employed leading to formation of apatite in the cathode electrode after applying a current. A platinum coil bent is usually employed to provide a conductive cage to locate the organic scaffold (Naldoni *et al.*, 2011). Electrodeposition led to the formation of HAp flat crystals on the outer surface of the scaffold, a morphology that contrast with the core-shell constructs usually obtained by a conventional SBF incubation processes (He *et al.*, 2014) (Fig. 12).

3D printing technologies are currently been developed for the preparation of scaffolds with complex geometries, being also appropriated to reproduce bone defect shapes (Trombetta *et al.*, 2017) (Fig. 13).

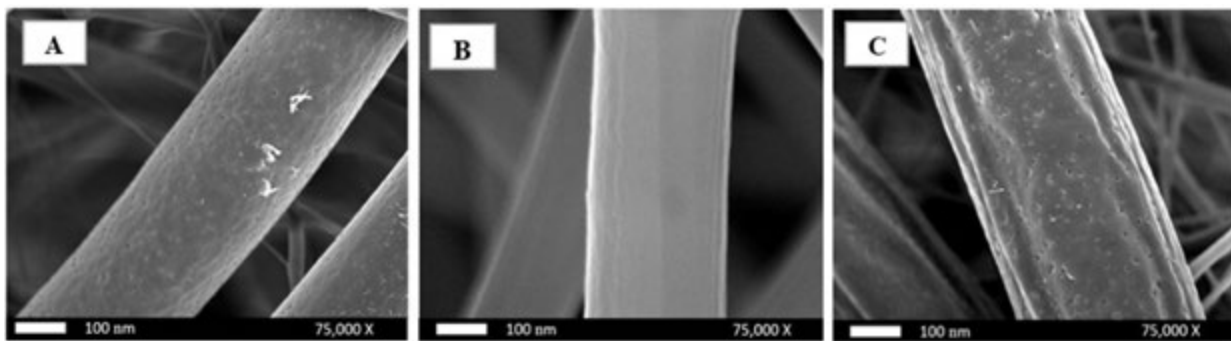


Fig. 12 SEM micrographs showing the porous structure of pristine PLA (A) and core/shell-structured PVA/PLA (C) and the pristine PVA (B). Reproduced with permission from Alharbi, H.F., Luqman, M., Khalil, K.A., *et al.*, 2018. Fabrication of core-shell structured nanofibers of poly (lactic acid) and poly (vinyl alcohol) by coaxial electrospinning for tissue engineering. *European Polymer Journal* 98, 483–491.

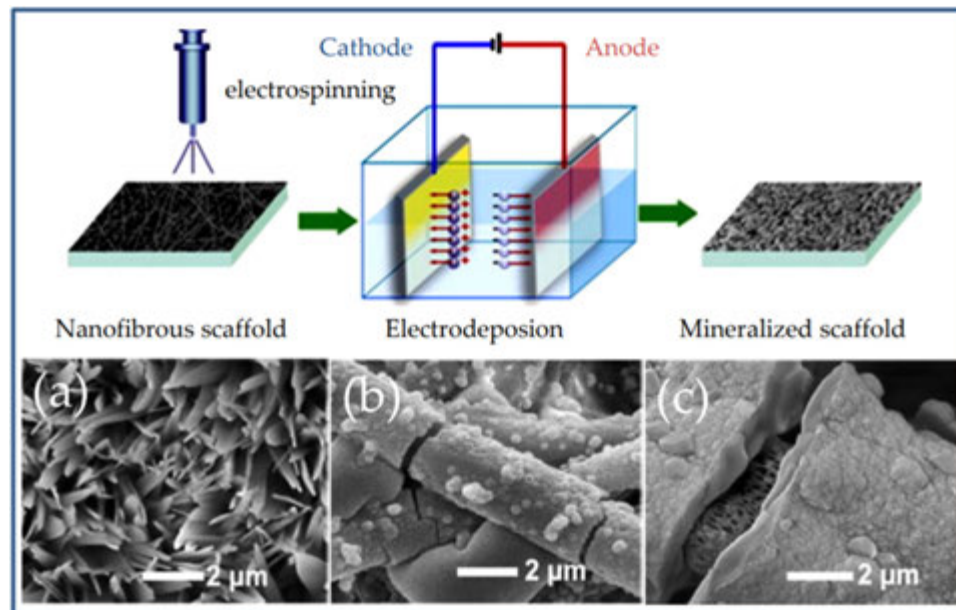


Fig. 13 Scheme showing the combined electrospinning/electrodeposition process to produce mineralized scaffolds. SEM micrographs corresponds to a PLA mineralized scaffold obtained by the electrodeposition method (a) and mineralized PLA scaffolds prepared by immersion in SBF fluid for 12 (b) and 30 (c) days. Reproduced with permission from He, C., Jin, X., Ma, P.X., 2014. Calcium phosphate deposition rate, structure and osteoconductivity on electrospun poly(L-lactic acid) matrix using electrodeposition or simulated body fluid incubation. *Acta Biomaterialia* 10, 419–427.

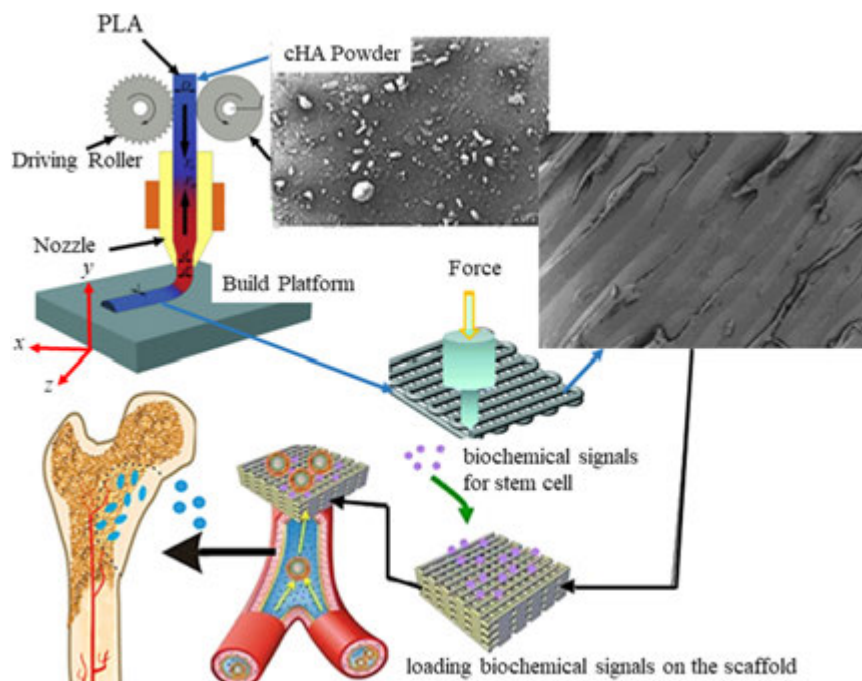


Fig. 14 Scheme showing the modeling of PLA scaffolds incorporating carbonated hydroxyapatite (cHA) by the FDM technology and the subsequent loading of biochemical signals. Reproduced with permission from Oladapo, B.I., Ismail, S.O., Zahedi, M., Khan, A., Usman, H., 2020. 3D printing and morphological characterization of polymeric composite scaffolds. *Engineering Structures* 216, 110752.

High accuracy 3D structures can be prepared by stereolithography if there are available appropriated liquid resins suitable of solidify by postcuring with a light source. HAp can be incorporated in the resins in order to enhance bioactivity. Thus, photo crosslinkable poly(D,L-lactide) having diacrylate groups has been successfully employed, being the stiffness of the cured resin dependent on the amount of incorporated HAp (Ronca *et al.*, 2013).

Different examples can be mentioned about the preparation of 3D biopolymer hybrid scaffolds by means of fusion and deposition modeling (FDM), using a continuous thermoplastic polymer filament. This technology is, economic, fast and suitable for manufacturing complex systems. Scaffolds constituted by PLA and carbonated hydroxyapatite (cHA) were found suitable for the treatment of cranial defects (Balogun and Oladapo, 2016) and in general for bone tissue regeneration (Oladapo *et al.*, 2020) (Fig. 14). The amount of loaded HAp could be successfully increased up to 50 wt% (Corcione *et al.*, 2019). Blends of PLA/CS incorporating HAp have also been processed by FDM (Ranjan *et al.*, 2019).

Selective laser sintering (SLS) has also been applied to fabricate BCP-based scaffolds for tissue engineering applications (Zeng *et al.*, 2020). Materials were biocompatible, favored cell adhesion, had osteogenic and healing potential.

Conclusions

Hydroxyapatite is a calcium phosphate with a high chemical similarity to bone, teeth and cartilages. Excellent biocompatibility, bioactivity and osteoconductive properties make HAp an essential material for hard tissue repair and replacement. Furthermore, biomedical applications can be extended to coatings, hydrogels, scaffolds, and carriers for drug, growth factor and gene delivery.

The interest on HAp nanoparticles is continuously growing due to their absorption and encapsulation capabilities. Furthermore, HAp nanoparticles can act as a "Trojan Horse" since they can be easily endocytized by cells where subsequently can deliver drugs or genes. In addition, HAp is a polyvalent substrate that can incorporate both ions and molecules giving rise to nanoparticles with antimicrobial activity.

The low strength of HAp is a limitation that precludes the manufacturing of implants constituted integrally by this inorganic material. Therefore, scaffolds employed in tissue engineering correspond to nanocomposites where natural (e.g., gelatin, ALG and CS) and synthetic (e.g., PLA, PLGA and PCL) polymers constituted the biodegradable matrix. Great efforts have recently been focused to develop three dimensional biomimetic materials with tuneable characteristics regarding porosity (e.g., pore size and interconnectivity), degradation rate, mechanical properties, bioactivity and resorption rate. Despite the enormous advances on tissue engineering there are still clear technological limitations for reproducing complex tissues. Conventional processes (e.g., electrospinning and phase separation) had reduced reproducibility and low cell deposition accuracy. 3D technologies showed a great potential but are still far from ideal to recreate complex systems. Capacity of new biocomposites to fulfill their promising expectations after implantation in large bone defects under constant and high stress should be verified.

New strategies are being opened thanks to the great potential of nanotechnology. Thus, surface nanotopographic modifications for the regulation of cell differentiation or advances on peptide self-assembling to render physical cross-linkable gels merit attention. In any case, new insights in the comprehension of the interactions between cells and biomaterials appear fundamental to develop suitable materials for clinical treatment.

Acknowledgments

The authors acknowledge support from MINECO and FEDER (Project RTI2018–101827-B-I009), and the Generalitat de Catalunya for the grant 2017SGR373.

References

- Alharbi, H.F., Luqman, M., Khalil, K.A., *et al.*, 2018. Fabrication of core-shell structured nanofibers of poly (lactic acid) and poly (vinyl alcohol) by coaxial electrospinning for tissue engineering. *European Polymer Journal* 98, 483–491.
- Alkilzy, M., Santamaria, R.M., Schmoeckel, J., Splieth, C.H., 2018. Treatment of carious lesions using self-assembling peptides. *Advances in Dental Research* 29, 42–47.
- Amini, A.R., Laurencin, C.T., Nukavarapu, S.P., 2012. Bone tissue engineering: Recent advances and challenges. *Critical Reviews in Biomedical Engineering* 40, 363–408.
- Ao, C., Niu, Y., Zhang, X., *et al.*, 2017. Fabrication and characterization of electrospun cellulose/nano-hydroxyapatite nanofibers for bone tissue engineering. *International Journal of Biological Macromolecules* 97, 568–573.
- Arinze, T.L., Tran, T., Mcalary, J., Daculsi, G., 2005. A comparative study of biphasic calcium phosphate ceramics for human mesenchymal stem-cell-induced bone formation. *Biomaterials* 26, 3631–3638.
- Aronov, D., Karlov, A., Rosenman, G., 2007. Hydroxyapatite nanoceramics: Basic physical properties and biointerface modification. *Journal of the European Ceramic Society* 27, 4181–4186.
- Balogun, V.A., Oladapo, B.I., 2016. Electrical energy demand modeling of 3D printing technology for sustainable manufacture. *International Journal of Engineering* 29, 954–961.
- Barco, A., Ingham, E., Fisher, J., Fermor, H., Davies, R.P.W., 2018. On the design and efficacy assessment of self-assembling peptide-based hydrogel-glycosaminoglycan mixtures for potential repair of early stage cartilage degeneration. *Journal of Peptide Science* 24, e3114.
- Bharadwaz, A., Jayasuriya, A.C., 2010. Recent trends in the application of widely used natural and synthetic polymer nanocomposites in bone tissue regeneration. *Materials Science & Engineering C* 110.110698.
- Bhuiyan, D.B., Jablonsky, M.J., Kolesov, I., *et al.*, 2015. Novel synthesis and characterization of a collagen-based biopolymer initiated by hydroxyapatite nanoparticles. *Acta Biomaterialia* 15, 181–190.
- Bisht, S., Bhakta, G., Mitra, S., Maitra, A., 2005. pDNA loaded calcium phosphate nanoparticles: Highly efficient non-viral vector for gene delivery. *International Journal of Pharmaceutics* 288, 157–168.
- Bohner, M., 2000. Calcium orthophosphates in medicine: From ceramics to calcium phosphate cements. *Injury* 31 (Suppl. 4), 37–47.
- Botchwey, E.A., Dupree, M.A., Pollack, S.R., Levine, E.M., Laurencin, C.T., 2003. Tissue engineered bone: Measurement of nutrient transport in three dimensional matrices. *Journal of Biomedical Materials Research A* 67, 357–367.
- Brown, W.E., Huey, D.J., Hu, J.C., Athanasios, K.A., 2018. Functional self-assembled neocartilage as part of a biphasic osteochondral construct. *PLOS One* 13.e0195261.
- Callister, W.D., Rethwisch, D.G., 2009. *Materials Science and Engineering: An Introduction*. Hoboken, NJ: John Wiley & Sons, Inc.
- Cao, M., Wang, Y., Guo, C., Qi, Y., Hu, C., 2004. Preparation of ultrahigh-aspect-ratio hydroxyapatite nanofibers in reverse micelles under hydrothermal conditions. *Langmuir* 20, 4784–4786.
- Carino, A., Ludwig, C., Cervellino, A., Müller, E., Testino, A., 2018. Formation and transformation of calcium phosphate phases under biologically relevant conditions: Experiments and modelling. *Acta Biomaterialia* 74, 478–488.
- Chae, T., Yang, H., Leung, V., Ko, F., Troczynski, T., 2013. Novel biomimetic hydroxyapatite/alginate nanocomposite fibrous scaffolds for bone tissue regeneration. *Journal of Materials Science: Materials in Medicine* 24, 1885–1894.
- Chang, W., Mu, X., Zhu, X., *et al.*, 2013. Biomimetic composite scaffolds based mineralization of hydroxyapatite on electrospun calcium-containing poly(vinyl alcohol) nanofibers. *Materials Science and Engineering* 33, 4369–4376.
- Chen, S., Hao, Y., Cui, W., Chang, J., Zhou, Y., 2013a. Biodegradable electrospun PLLA/chitosan membrane as guided tissue regeneration membrane for treating periodontitis. *Journal Materials Science* 48, 6567–6577.
- Chen, Y., Kawazoe, N., Chen, G., 2018. Preparation of dexamethasone-loaded biphasic calcium phosphate nanoparticles/collagen porous composite scaffolds for bone tissue engineering. *Acta Biomaterialia* 67, 341–353.
- Chen, Y., Yang, L., Huang, S., *et al.*, 2013b. Delivery system for DNazymes using arginine-modified hydroxyapatite nanoparticles for therapeutic application in a nasopharyngeal carcinoma model. *Journal of Nanomedicine* 8, 3107–3118.
- Chowdhury, E.H., 2011. Fluoride enhances transfection activity of carbonate apatite by increasing cytoplasmic stability of plasmid DNA. *Biochemical Biophysical Research Communications* 409, 745–747.
- Chowdhury, E.H., Kunou, M., Nagaoka, M., *et al.*, 2004. High-efficiency gene delivery for expression in mammalian cells by nanoprecipitates of Ca–Mg phosphate. *Gene* 341, 77–82.
- Corcione, C.E., Gervaso, F., Scalera, F., *et al.*, 2019. Highly loaded hydroxyapatite microsphere/PLA porous scaffolds obtained by fused deposition modelling. *Ceramics International* 45, 2803–2810.
- Cui, X., Liang, T., Liu, C., Yuan, Y., Qian, J., 2016. Correlation of particle properties with cytotoxicity and cellular uptake of hydroxyapatite nanoparticles in human gastric cancer cells. *Materials Science and Engineering C* 67, 453–460.
- Dorozhkin, S.V., 2016. Multiphasic calcium orthophosphate (CaPO₄) bioceramics and their biomedical applications. *Ceramics International* 42, 6529–6554.
- Dorozhkin, S.V., Dorozhkin, S.V., 2002. Mechanism of the solid-state transformation of a calcium-deficient hydroxyapatite (CDHA) into biphasic calcium phosphate (BCP) at elevated temperatures. *Chemical Materials* 14, 4267–4272.
- Doshi, J., Reneker, D.H., 1995. Electrospinning process and applications of electrospun fibers. *Journal of Electrostatics* 35, 151–160.
- Dou, X.C., Zhu, X.P., Zhou, J., *et al.*, 2011. Minocycline-released hydroxyapatite-gelatin nanocomposite and its cytocompatibility in vitro. *Biomedical Materials* 6, 025002.
- Dou, Y., Cai, S., Ye, X., *et al.*, 2012. Preparation of mesoporous hydroxyapatite films used as biomaterials via sol-gel technology. *Journal of Sol-Gel Science and Technology* 61, 126–132.
- Elkassas, D., Arafa, A., 2017. The innovative applications of therapeutic nanostructures in dentistry. *Nanomedicine* 13, 1543–1562.
- Elliott, J.C., 1994. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*. Studies in Inorganic Chemistry. 18. Amsterdam: Elsevier, p. 389.

- Fabbri, F., Bondioli, F., Messori, M., *et al.*, 2010. Porous scaffolds of polycaprolactone reinforced with in situ generated hydroxyapatite for bone tissue engineering. *Journal of Materials Science: Materials in Medicine* 21, 343–351.
- Ferraz, M.P., Mateus, A.Y., Sousa, J.C., Monteiro, F.J., 2007. Nanohydroxyapatite microspheres as delivery system for antibiotics: Release kinetics, antimicrobial activity, and interaction with osteoblasts. *Journal Biomedical Materials Research Part A* 81, 994–1004.
- Fu, S., Ni, P., Wang, B., *et al.*, 2012. In vivo biocompatibility and osteogenesis of electrospun poly(ϵ -caprolactone)-poly(ethylene glycol)-poly(ϵ -caprolactone)/nano-hydroxyapatite composite scaffold. *Biomaterials* 33, 8363–8371.
- Fuertes, A., Juanes, M., Granja, J.R., Montenegro, J., 2017. Supramolecular functional assemblies: Dynamic membrane transporters and peptide nanotubular composites. *Chemical Communications* 53, 7861–7871.
- Fukumoto, S., Kiba, T., Hall, B., *et al.*, 2004. Ameloblastin is a cell adhesion molecule required for maintaining the differentiation state of ameloblasts. *Journal of Cell Biology* 167, 973–983.
- Garai, S., Sinha, A., 2014. Biomimetic nanocomposites of carboxymethyl cellulose-hydroxyapatite: Novel three dimensional load bearing bone grafts. *Colloids and Surfaces B: Biointerfaces* 115, 182–190.
- Goyal, A.K., Khatri, K., Mishra, N., *et al.*, 2009. Development of self-assembled nanoceramic carrier construct(s) for vaccine delivery. *Journal of Biomaterials Applications* 24, 65–84.
- Halima, N.B., 2016. Poly(vinyl alcohol): Review of its promising applications and insights into biodegradation. *RSC Advances* 6, 32823–32832.
- Halifi, A., Fathi, M.H., Sadeghi, H.M.M., 2010. Effect of strontium ions substitution on gene delivery related properties of calcium phosphate nanoparticles. *Journal Materials Science: Materials in Medicine* 21, 2601–2609.
- Hartgerink, J.D., Beniash, E., Stupp, S.I., 2001. Self-assembly and mineralization of peptide-amphiphile nanofibers. *Science* 294, 1684–1688.
- Hartgerink, J.D., Beniash, E., Stupp, S.I., 2002. Peptide-amphiphile nanofibers: A versatile scaffold for the preparation of self-assembling materials. *Proceedings of the National Academy of Sciences of the United States of America* 99, 5133–5138.
- He, C., Jin, X., Ma, P.X., 2014. Calcium phosphate deposition rate, structure and osteoconductivity on electrospun poly(L-lactic acid) matrix using electrodeposition or simulated body fluid incubation. *Acta Biomaterialia* 10, 419–427.
- He, L., Zhang, Y., Zeng, X., *et al.*, 2009. Fabrication and characterization of poly(L-lactic acid)3D nanofibrous scaffolds with controlled architecture by liquid-liquid phase separation from a ternary polymer-solvent system. *Polymer* 50, 4128–4138.
- Holt, K.B., Bard, A.J., 2005. Interaction of silver (I) ions with the respiratory chain of *Escherichia coli*: An electrochemical and scanning electrochemical microscopy study of the antimicrobial mechanism of micromolar Ag^+ . *Biochemistry* 44, 13214–13223.
- Hong, Z., Qiu, X., Sun, J., *et al.*, 2004. Grafting polymerization of L-lactide on the surface of hydroxyapatite nano-crystals. *Polymer* 45, 6699–6706.
- Hori, A., Wang, X., Gelain, F., Zhang, S., 2007. Biological designer self-assembling peptide nanofiber scaffolds significantly enhance osteoblast proliferation, differentiation and 3-D migration. *PLOS One* 2.e190.
- Hu, C., Guo, J., Qu, J.H., Hu, X.X., 2007. Efficient destruction of bacteria with Ti(IV) and antibacterial ions in co-substituted hydroxyapatite films. *Applied Catalysis B: Environmental* 73, 345–353.
- Huang, Y.T., Imura, M., Nemoto, Y., Cheng, C.H., Yamauchi, Y., 2011. Block-copolymer-assisted synthesis of hydroxyapatite nanoparticles with high surface area and uniform size. *Science and Technology of Advanced Materials* 12, 045005.
- Huang, Z., Newcomb, C.J., Bringas Jr., P., Stupp, S.I., Sneed, M.L., 2010. Biological synthesis of tooth enamel by an artificial matrix. *Biomaterials* 31, 9202–9211.
- Hwang, S.J., Lee, J.S., Ryu, T.K., *et al.*, 2016. Alendronate-modified hydroxyapatite nanoparticles for bone-specific dual delivery of drug and bone mineral. *Macromolecular Research* 24, 623–628.
- Kalita, S.J., Bhardwaj, A., Bhatt, H.A., 2007. Nanocrystalline calcium phosphate ceramics in biomedical engineering. *Materials Science and Engineering C* 27, 441–449.
- Katta, J., Stapleton, T., Ingham, E., Jin, Z., Fisher, J., 2008. The effect of glycosaminoglycan depletion on the friction and deformation of articular cartilage. *Proceedings of the Institution of Mechanical Engineers H* 222, 1–11.
- Kay, M.I., Young, R.A., Posner, A.S., 1964. Crystal structure of hydroxyapatite. *Nature* 204, 1050–1052.
- Kim, J.S., Kuk, E., Yu, K., *et al.*, 2007. Antimicrobial effects of silver nanoparticles. *Nanomedicine: Nanotechnology, Biology and Medicine* 3, 95–101.
- Kim, K.W., Lee, H.H., Knowles, J.C., 2006. Electrospinning biomedical nanocomposite fibers of hydroxyapatite/poly(lactic acid) for bone regeneration. *Journal Biomedical Materials Research Part A* 79, 643–649.
- Kisiday, J., Jin, M., Kurz, B., *et al.*, 2002. Self-assembling peptide hydrogel fosters chondrocyte extracellular matrix production and cell division: Implications for cartilage tissue repair. *Proceedings of the National Academy of Sciences of the United States of America* 99, 9996–10001.
- Kisiday, J.D., Colbath, A.C., Tangtrongsup, S., 2018. Effect of culture duration on chondrogenic preconditioning of equine bone marrow mesenchymal stem cells in self-assembling peptide hydrogel. *Journal of Orthopaedic Research* 37, 1368–1375.
- Kobayashi, T., Ono, S., Hirakura, S., Oaki, Y., Imai, H., 2012. Morphological variation of hydroxyapatite grown in aqueous solution based on simulated body fluid. *Crystal Engineering Communications* 14, 1143–1149.
- Koupaei, N., Karkhaneh, A., 2016. Porous crosslinked polycaprolactone hydroxyapatite networks for bone tissue engineering. *Tissue Engineering and Regenerative Medicine* 13, 251–260.
- Kwong, F.N.K., Harris, M.B., 2008. Recent developments in the biology of fracture repair. *Journal of the American Academy of Orthopaedic Surgeons* 16 (11), 619–625.
- Langer, R., Vacanti, J.P., 1993. Tissue engineering. *Science* 260, 920–926.
- Layrolle, P., Lebugle, A., 1994. Characterization and reactivity of nanosized calcium phosphates prepared in anhydrous ethanol. *Chemical Materials* 6, 1996–2004.
- Lee, K., Oh, M.H., Lee, M.S., *et al.*, 2013a. Stabilized calcium phosphate nano-aggregates using a dopa-chitosan conjugate for gene delivery. *International Journal of Pharmaceutics* 445, 196–202.
- Lee, W.H., Loo, C.Y., Van, K.L., Zavgorodniy, A.V., Rohanizadeh, R., 2012. Modulating protein adsorption onto hydroxyapatite particles using different amino acid treatments. *Journal of the Royal Society Interface* 9, 918–927.
- Lee, W.H., Loo, C.Y., Zavgorodniy, A.V., Ghadiri, M., Rohanizadeh, R., 2013b. A novel approach to enhance protein adsorption and cell proliferation on hydroxyapatite: Citric acid treatment. *RSC Advances* 3, 4040–4051.
- Lee, W.L., Loo, C.Y., Rohanizadeh, R., 2014. A review of chemical surface modification of bioceramics. Effects on protein adsorption and cellular response. *Colloids and Surfaces B: Biointerfaces* 122, 823–834.
- Li, B., Guo, B., Fan, H.S., Zhang, X.D., 2008. Preparation of nano-hydroxyapatite particles with different morphology and their response to highly malignant melanoma cells in vitro. *Applied Surface Science* 255, 357–360.
- Lim, P.N., Chang, L., Thian, E.S., 2015. Development of nanosized silver-substituted apatite for biomedical applications: A review. *Nanomedicine: Nanotechnology, Biology and Medicine* 2015 (11), 1331–1344.
- Liu, C., He, H., 2017. *Development s and Applications of Calcium Phosphates Bone Cements*. Singapore: Springer.
- Liu, S., Sun, Y., Fu, *et al.*, 2016. Bioinspired collagen-apatite nanocomposites for bone regeneration. *Journal of Endodontics* 42, 1226–1232.
- Liu, T.Y., Chen, S.Y., Li, J.H., Liu, D.M., 2006. Study on drug release behavior of CDHA/chitosan nanocomposites – Effect of CDHA nanoparticles. *Journal Controlled Release* 112, 88–95.
- Liu, Y., Lu, Y., Tian, X., *et al.*, 2009. Segmental bone regeneration using an rhBMP-2-loaded gelatin/nanohydroxyapatite/fibrin scaffold in a rabbit model. *Biomaterials* 30, 6276–6285.

- Liu, Y., Cui, H., Zhuang, X., *et al.*, 2013. Nanohydroxyapatite surfaces grafted with electroactive aniline tetramers for bone-tissue engineering. *Macromolecular Bioscience* 13, 356–365.
- Liu, Z.S., Tang, S.L., Ai, Z.L., 2003. Effects of hydroxyapatite nanoparticles on proliferation and apoptosis of human hepatoma BEL-7402 cells. *World Journal of Gastroenterology* 9, 1968–1971.
- López-Macipe, A., Gómez-Morales, J., Rodríguez-Clemente, R., 1998. Nanosized hydroxyapatite precipitation from homogeneous calcium/citrate/phosphate solutions using microwave and conventional heating. *Advanced Materials* 10, 49–53.
- Luo, H., Li, W., Ji, D., *et al.*, 2016. One-step exfoliation and surface modification of lamellar hydroxyapatite by intercalation of glucosamine. *Materials Chemistry and Physics* 173, 262–267.
- Ma, M.G., 2012. Hierarchically nanostructured hydroxyapatite: Hydrothermal synthesis, morphology control, growth mechanism, and biological activity. *International Journal of Nanomedicine* 7, 1781–1791.
- Ma, M.G., Zhu, J.F., 2009. Solvothermal synthesis and characterization of hierarchically nanostructured hydroxyapatite hollow spheres. *European Journal Inorganic Chemistry* 36, 5522–5526.
- Ma, P.X., 2004. Scaffolds for tissue fabrication. *Materials Today* 7, 30–40.
- Ma, X., He, Z., Han, F., *et al.*, 2016. Preparation of collagen/hydroxyapatite/alendronate hybrid hydrogels as potential scaffolds for bone regeneration. *Colloids and Surfaces B: Biointerfaces* 143, 81–87.
- Maehara, H., Sotome, S., Yoshii, T., *et al.*, 2010. Repair of large osteochondral defects in rabbits using porous hydroxyapatite/collagen (HAp/Col) and fibroblast growth factor-2 (FGF-2). *Journal of Orthopaedic Research* 28, 677–686.
- Manjubala, I., Sastry, T.P., Suresh Kumar, R.V., 2005. Bone in-growth induced by biphasic calcium phosphate ceramic in femoral defect of dogs. *Journal of Biomaterials Applied* 19, 341–360.
- Mankani, M.H., Afghani, S., Franco, J., *et al.*, 2011. Lamellar spacing in cuboid hydroxyapatite scaffolds regulates bone formation by human bone marrow stromal cells. *Tissue Engineering Part A* 17, 1615–1623.
- Mason, C., Dunnill, P., 2008. A brief definition of regenerative medicine. *Regenerative Medicine* 2008 (3), 1–5.
- Mathew, M., Takagi, S., 2001. Structures of biological minerals in dental research. *Journal of Research of the National Institute of Standards and Technology* 106, 1035–1044.
- McNally, M.A., Ferguson, J.Y., Lau, A.C.K., *et al.*, 2016. Single-stage treatment of chronic osteomyelitis with a new absorbable, gentamicin-loaded, calcium sulphate/hydroxyapatite biocomposite: A prospective series of 100 cases. *Bone & Joint Journal* 98, 1289–1296.
- Monteiro, M.M., Rocha, N.C.C., Rossi, A.M., Soares, G.A., 2003. Dissolution properties of calcium phosphate granules with different compositions in simulated body fluid. *Journal Biomedical Material Research* 65, 299–305.
- Munarín, F., Petrini, P., Gentilini, R., *et al.*, 2015. Micro- and nano-hydroxyapatite as active reinforcement for soft biocomposites. *International Journal of Biological Macromolecules* 72, 199–209.
- Naldoni, A., Minguzzi, A., Vertova, A., *et al.*, 2011. Electrochemically assisted deposition on TiO₂ scaffold for T issue engineering: An apatite bio-inspired crystallization pathway. *Materials Chemistry* 21, 400–407.
- Naudot, M., Garcia Garcia, A., Jankovsky, N., *et al.*, 2020. The combination of a poly-caprolactone/nano-hydroxyapatite honeycomb scaffold and mesenchymal stem cells promotes bone regeneration in rat calvarial defects. *Journal of Tissue Engineering and Regenerative Medicine* 14 (11), doi:10.1002/term.3114.
- Nazeer, M.A., Yilgör, E., Yilgör, I., 2017. Intercalated chitosan/hydroxyapatite nanocomposites: Promising materials for bone tissue engineering applications. *Carbohydrate Polymers* 175, 38–46.
- Nonoyama, T., Ogasawara, H., Tanaka, M., Higuchi, M., Kinoshita, T., 2012. Calcium phosphate biomineralization in peptide hydrogels for injectable bone-filling materials. *Soft Matter* 8, 11531–11536.
- Ogose, A., Hotta, T., Kawashima, H., *et al.*, 2005. Comparison of hydroxyapatite and beta tricalcium phosphate as bone substitutes after excision of bone tumors. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 72B, 94–101.
- Oladapo, B.I., Ismail, S.O., Zahedi, M., Khan, A., Usman, H., 2020. 3D printing and morphological characterisation of polymeric composite scaffolds. *Engineering Structures* 216.110752.
- Paine, M.L., White, S.N., Luo, W., *et al.*, 2001. Regulated gene expression dictates enamel structure and tooth function. *Matrix Biology* 20, 273–292.
- Palena, C., Abrams, S.I., Schlom, J., Hodge, J.W., 2006. Cancer vaccines: Preclinical studies and novel strategies. *Advances in Cancer Research* 95, 115–145.
- Pang, Y.X., Bao, X., 2003. Influence of temperature, ripening time and calcination on the morphology and crystallinity of hydroxyapatite nanoparticles. *Journal of the European Ceramic Society* 23, 1697–1704.
- Peters, F., Reif, D., 2004. Functional materials for bone regeneration from beta-tricalcium phosphate. *Materials Science and Engineering Technology* 35, 203–207.
- Phipps, M.C., Xu, Y.Y., Bellis, S.L., 2012. Delivery of platelet-derived growth factor as a chemotactic factor for mesenchymal stem cells by bone-mimetic electrospun scaffolds. *PLOS One* 7.e40831.
- Pighinelli, L., Kucharska, M., 2013. Chitosan–hydroxyapatite composites. *Carbohydrate Polymers* 93, 256–262.
- Pradal, C., Kithva, P., Martin, D., Trau, M., Grondahl, L., 2011. Improvement of the wettensile properties of nanostructured hydroxyapatite and chitosan biocomposite films through hydrophobic modification. *Journal of Material Chemistry* 21, 2330–2337.
- Prajatelistia, E., Lim, C., Oh, D.X., Jun, S.H., Hwang, D.S., 2015. Chitosan and hydroxyapatite composite crosslinked by dopamine has improved anisotropic hydroxyapatite growth and wet mechanical properties. *Engineering in Life Sciences* 15, 254–261.
- Qui, Q., Yao, Y., Jia, X., *et al.*, 2019. Effects of polyethylene glycol content on the properties of a silk fibroin/nano-hydroxyapatite/polyethylene glycol electrospun scaffold. *RSC Advances* 9, 33941–33948.
- Ranjan, N., Singh, R., Ahuja, I., 2019. Investigations for mechanical properties of PLA-HAP-CS based functional prototypes. *Materials Today Processing* 18, 2329–2334.
- Rao, K.P., 1995. Recent developments of collagen-based materials for medical applications and drug delivery systems. *Journal of Biomaterials Science, Polymer Edition* 7, 623–645.
- Raspa, A., Saracino, G.A.A., Pugliese, R., *et al.*, 2014. Complementary co-assembling peptides: From in silico studies to in vivo application. *Advanced Functional Materials* 24, 6317–6328.
- Rechendorff, K., Hovgaard, M.B., Foss, M., Zhdanov, V.P., Besenbacher, F., 2006. Enhancement of protein adsorption induced by surface roughness. *Langmuir* 22(22), 10885–10888.
- Ren, F., Leng, Y., Ding, Y., Wang, K., 2013. Hydrothermal growth of biomimetic carbonated apatite nanoparticles with tunable size, morphology and ultrastructure. *Crystal Engineering Communications* 15, 2137–2146.
- Revilla-López, G., Casanovas, J., Bertran, O., *et al.*, 2013. Modeling biominerals formed by apatites and DNA. *Biointerphases* 8, 10.
- Rivas, M., del Valle, L.J., Rodríguez-Rivero, A.M., *et al.*, 2018. Loading of antibiotic into biocoated hydroxyapatite nanoparticles: Smart antitumor platforms with regulated release. *ACS Biomaterials* 4, 3234–3245.
- Rivas, M., Pelecha, M., Franco, L., *et al.*, 2019b. Incorporation of chloramphenicol loaded hydroxyapatite nanoparticles into polylactide. *International Journal of Molecular Sciences* 20.5056.
- Rivas, M., del Valle, L.J., Alemán, Puiggalí, J., 2019a. Peptide self-assembly into hydrogels for biomedical applications related to hydroxyapatite. *Gels* 5, 14.
- Romanelli, S.M., Fath, K.R., Phekoo, A.P., Knoll, G.A., Barnejee, I.A., 2015. Layer-by-layer assembly of peptide based bioorganic–inorganic hybrid scaffolds and their interactions with osteoblastic MC3T3-E1 cells. *Materials Science and Engineering C* 51, 316–328.

- Ronca, A., Ambrosio, Grijpma, D.W., 2013. Preparation of designed poly(D,L-lactide)/nanosized hydroxyapatite composite structures by stereolithography. *Acta Biomaterialia* 9, 5989–5996.
- Roveri, N., Iafisco, M., 2010. Evolving application of biomimetic nanostructured hydroxyapatite. *Nanotechnology, Science and Applications* 3, 107–125.
- Saha, S.K., Banerjee, A., Banerjee, S., Bose, S., 2009. Synthesis of nanocrystalline hydroxyapatite using surfactant template systems: Role of templates in controlling morphology. *Materials Science Engineering C* 29, 2294–2301.
- Sailaja, G.S., Sreenivasan, K., Yokogawa, Y., Kumary, T.V., Varma, H.K., 2009. Bioinspired mineralization and cell adhesion on surface functionalized poly(vinyl alcohol) films. *Acta Biomaterialia* 5, 1647–1655.
- Santos, J.L., Pandita, D., Rodrigues, J., *et al.*, 2011. Non-viral gene delivery to mesenchymal stem cells: Methods, strategies and application in bone tissue engineering and regeneration. *Current Gene Therapy* 11, 46–57.
- Shi, P., Zuo, Y., Li, X., *et al.*, 2010. Gentamicin-impregnated chitosan/nanohydroxyapatite/ethyl cellulose microspheres granules for chronic osteomyelitis therapy. *Journal Biomedical Materials Research Part A* 93, 1020–1031.
- Shor, L., Gucer, S., Wen, X., Gandhi, M., Sun, W., 2007. Fabrication of three-dimensional polycaprolactone/hydroxyapatite tissue scaffolds and osteoblast-scaffold interactions in vitro. *Biomaterials* 28, 5291–5297.
- Shum, H.C., Bandyopadhyay, A., Bose, S., Weitz, D.A., 2009. Double emulsion droplets as microreactors for synthesis of mesoporous hydroxyapatite. *Chemical Materials* 21, 5548–5555.
- Sokolova, V.V., Radtke, I., Heumann, R., Apple, M., 2006. Effective transfection of cells with multi-shell calcium phosphate-DNA nanoparticle. *Biomaterials* 27, 3147–3153.
- Song, W., Markel, D.C., Wang, S., *et al.*, 2012. Electrospun poly(vinyl alcohol)-collagen-hydroxyapatite nanofibers: A biomimetic extracellular matrix for osteoblastic cells. *Nanotechnology* 23, 115101–115115.
- Song, W., Yu, X., Markel, D.C., Shi, T., Ren, W., 2013a. Coaxial PCL/PVA electrospun nanofibers: Osseointegration enhancer and controlled drug release device. *Biofabrication* 5, 035006.
- Song, X.F., Ling, F.G., Chen, X.S., 2013b. Grafting polymerization of L-lactide on the surface of hydroxyapatite nanoparticles. *Acta Polymerica Sinica* 1, 95–101.
- Sotome, S., Uemura, T., Kikuchi, M., *et al.*, 2004. Synthesis and in vivo evaluation of a novel hydroxyapatite/collagen–alginate as a bone filler and a drug delivery carrier of bone morphogenetic protein. *Material Science and Engineering* 24, 341–347.
- Stevens, M.M., 2008. Biomaterials for bone tissue engineering. *Materials Today* 11, 18–25.
- Stupp, S.I., 2005. Biomaterials for regenerative medicine. *MRS Bulletin* 30, 546–553.
- Sukhodub, L.B., Yanovska, G.O., Kuznetsov, V.M., Martynyuk, O.O., Sukhodub, L.F., 2016. Injectable biopolymer-hydroxyapatite hydrogels: Obtaining and their characterization. *Journal of Nano- and Electronic Physics* 8, 01032.
- Sun, R., Chen, K., Lu, Y., 2009. Fabrication and dissolution behavior of hollow hydroxyapatite microspheres intended for controlled drug release. *Materials Research Bulletin* 44, 1939–1942.
- Tang, W., Yuan, Y., Liu, C., *et al.*, 2014. Differential cytotoxicity and particle action of hydroxyapatite nanoparticles in human cancer cells. *Nanomedicine* 9, 397–412.
- Tang, Y.F., Liu, G.J., 2014. In vivo degradation behavior of porous composite scaffolds of poly(lactide-co-glycolide) and nano-hydroxyapatite surface grafted with poly(lactide). *Chinese Journal of Polymer Science* 32, 805–816.
- Tao, K., Levin, A., Adler-Abramovich, L., Gazit, E., 2016. Fmoc-modified amino acids and short peptides: Simple bio-inspired building blocks for the fabrication of functional materials. *Chemical Society Reviews* 45, 3935–3953.
- Thangavelu, M., Narasimha, R.R., Adithan, A., *et al.*, 2016. Reengineered graft copolymers as a potential alternative for the bone tissue engineering application by inducing osteogenic markers expression and biocompatibility. *Colloids and Surfaces B: Biointerfaces* 143, 15–26.
- Thien, D.V.H., Hsiao, S.W., Ho, M.H., Li, C.H., Shih, J.L., 2013. Electrospun chitosan/hydroxyapatite nanofibers for bone tissue engineering. *Journal Materials Science* 48, 1640–1645.
- Tierney, E.G., Duffy, G.P., Cryan, S.A., Curtin, C.M., O'Brien, F.J., 2013. Non-viral gene-activated matrices: Next generation constructs for bone repair. *Organogenesis* 9, 22–28.
- Tong, H.W., Wang, M., Li, Z.Y., Lu, W.W., 2010. Electrospinning, characterization and in vitro biological evaluation of nano-composite fibers containing carbonated hydroxyapatite nanoparticles. *Biomedical Materials* 5, 054111.
- Trombetta, R., Inzana, J.A., Schwarz, E.M., Kates, S.L., Awad, H.A., 2017. 3D printing of calcium phosphate ceramics for bone tissue engineering and drug delivery. *Annals of Biomedical Engineering* 45, 23–44.
- Tsukamoto, J., Naruse, K., Nagai, Y., *et al.*, 2017. Efficacy of a self-assembling peptide hydrogel, SPG-178-gel, for bone regeneration and three-dimensional osteogenic induction of dental pulp stem cells. *Tissue Engineering Part A* 23, 1394–1402.
- Turon, P., del Valle, L., Alemán, C., Puiggali, J., 2017. Biodegradable and biocompatible systems based on hydroxyapatite nanoparticles. *Applied Sciences* 6, 60.
- Venkatesan, P., Puvvada, N., Dash, R., *et al.*, 2011. The potential of celecoxib-loaded hydroxyapatite-chitosan nanocomposite for the treatment of colon cancer. *Biomaterials* 32, 3794–3806.
- Venugopal, J., Rajeswari, R., Shayanti, M., *et al.*, 2013. Electrospun hydroxyapatite on polymer nanofibers to differentiate mesenchymal stem cells to osteogenes. *Journal of Biomaterials Science, Polymer Edition* 24, 170–184.
- Wei, J., Liu, A., Chen, L., *et al.*, 2009. The surface modification of hydroxyapatite nanoparticles by the ring opening polymerization of γ -benzyl-L-glutamate N-carboxyanhydride. *Macromolecular Bioscience* 9, 631–638.
- Wei, J., Guo-Wang, P., Cui, L., *et al.*, 2014. Novel method to graft chitosan on the surface of hydroxyapatite nanoparticles via “click” reaction. *Chemical Research in Chinese Universities* 30, 1063–1065.
- Weiner, S., Wagner, H.D., 1998. The material bone: Structure mechanical function relations. *Annual Review of Materials Research* 28, 271–298.
- Welzel, T., Radtke, I., Meyer-Zaika, W., Heumann, R., Eppler, M., 2004. Transfection of cells with custom-made calcium phosphate nanoparticles coated with DNA. *Journal Materials Chemistry* 14, 2213–2217.
- Xia, Z., Liao, L., Zhao, S., 2009. Synthesis of mesoporous hydroxyapatite using a modified hard-templating route. *Materials Research Bulletin* 44, 1626–1629.
- Xiong, H., Du, S., Ni, J., Zhou, J., Yao, J., 2016. Mitochondria and nuclei dual-targeted heterogeneous hydroxyapatite nanoparticles for enhancing therapeutic efficacy of doxorubicin. *Biomaterials* 94, 70–83.
- Yang, D.J., Jeon, J.H., Lee, S.Y., *et al.*, 2016. Effects of collagen grafting on cell behaviors in BCP scaffold with interconnected pore structure. *Biomaterials Research* 20, 1–7.
- Yang, H.C., Hon, M.H., 2009. The effect of the molecular weight of chitosan nanoparticles and its application on drug delivery. *Microchemical Journal* 92, 87–91.
- Ye, F., Guo, H., Zhang, H., He, X., 2010. Polymeric micelle-templated synthesis of hydroxyapatite hollow nanoparticles for a drug delivery system. *Acta Biomaterialia* 6, 2212–2218.
- Yuan, Y., Liu, C., Qian, J., Wang, J., Zhang, Y., 2010. Size-mediated cytotoxicity and apoptosis of hydroxyapatite nanoparticles in human hepatoma HepG2 cells. *Biomaterials* 31, 730–740.
- Zakaria, S.M., Sharif Zein, S.H., Othman, M.R., Yang, F., Jansen, J.A., 2013. Nanophase hydroxyapatite as a biomaterial in advanced hard tissue engineering: a review. *Tissue Engineering Part B* 19, 431–441.
- Zeng, H., Pathak, J.L., Shi, J., *et al.*, 2020. Indirect selective laser sintering-printed microporous biphasic calcium phosphate scaffold promotes endogenous bone regeneration via activation of ERK1/2 signaling. *Biofabrication* 12, 025032.
- Zeugolis, D.I., Khew, S.T., Yew, E.S.Y., *et al.*, 2008. Electro-spinning of pure collagen nano-fibres—Just an expensive way to make gelatin? *Biomaterials* 29, 2293–2305.
- Zhang, C., Yang, J., Quan, Z., *et al.*, 2009. Hydroxyapatite nano- and microcrystals with multifunctional morphologies: Controllable synthesis and luminescence properties. *Crystal Growth & Design* 9, 2725–2733.

- Zhang, R., Ma, P.X., 1999. Poly(alpha hydroxyl acids)/hydroxyapatite porous composites for bone tissue engineering. I. Preparation and morphology. *Journal of Biomedical Material Research* 44, 446–455.
- Zhang, Z., Wu, G., Cao, Y., *et al.*, 2018. Self-assembling peptide and nHA/CTS composite scaffolds promote bone regeneration through increasing seed cell adhesion. *Materials Science and Engineering C* 93, 445–454.
- Zheng, H., 1997. Interaction mechanism in sol-gel transition of alginate solutions by addition of divalent cations. *Carbohydrate Research* 302, 97–101.
- Zhou, N., Liu, C., Lv, S., *et al.*, 2016. Degradation prediction model and stem cell growth of gelatin-PEG composite hydrogel. *Journal Biomedical Material Research Part A* 104, 3149–3156.
- Zhu, S.H., Huang, B.Y., Zhou, K.C., *et al.*, 2004. Hydroxyapatite nanoparticles as a novel gene carrier. *Journal Nanoparticle Research* 3, 307–311.
- Zuo, G., Wan, Y., Meng, X., *et al.*, 2011. Synthesis and characterization of a lamellar hydroxyapatite/DNA nanohybrid. *Materials Chemistry and Physics* 126, 470–475.
- Zuo, G.F., Wan, Y.Z., Xu, B., *et al.*, 2013. Synthesis and characterisation of laminated HA/PMMA nanocomposites by one-step intercalative bulk polymerisation. *Plastics Rubber and Composites* 42, 219–222.

Further Reading

- Panda, N.N., Jonnalagadda, S., Pramanik, K., 2013. Development and evaluation of cross-linked collagen-hydroxyapatite scaffolds for tissue engineering. *Journal of Biomaterials Science Polymer Edition* 24, 2031–2044.

Biopolymer Matrix Composite for Drug Delivery Applications in Cancer

Ankit Jain and Madhavi Tripathi, Indian Institute of Science, Bangalore, Karnataka, India

Shiv K Prajapati, Ram-Eesh Institute of Vocational and Technical Education, Greater Noida, Uttar Pradesh

Ashok M Raichur, Indian Institute of Science, Bangalore, Karnataka, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

Conventional Drug therapy for any illness follows the principle of attaining effective and desired plasma concentration of the therapeutic drug. Plasma concentration is reached by varying the frequency and dosage of the therapeutic molecules after the evaluation of their half-life. This approach heavily counts on the extensive use of drug molecules coated and compressed to manufacture capsules or tablets. The conventional form of drug therapy faces several limitations like rapid drug clearance, low bioavailability, low patient compliance, limited half-life, high toxicity and absence of selectivity. Developing a novel drug particle to surmount these barriers is time-consuming and pricey (Tiwari *et al.*, 2012). So, to solve the issues of conventional drugs, the investigators started exploring ways to ameliorate the efficiency and safety of generic medicines. Drug Delivery Systems (DDS) were thus worked upon for safer use of available drugs, to attain a better scope of selectivity, less toxicity and extended half-life. The introduction of DDS as a biologically suited structure for the targeted transportation of therapeutic factors got immense recognition lately. DDS acts as an interface connecting the patient and the active drug molecules. The drug delivery process follows the sequence of treatment with the therapeutic product followed by the discharge of the functional components from the product, and then the distribution of the functional components to the target site. It is advantageous, owing to its property of selectivity with a controlled rate of release (Patra *et al.*, 2018; Liu *et al.*, 2016a). Drug delivery applications are now being practiced for numerous diseases, including its extensive application for cancer research. Cancer is the second most cause of global mortality following cardiovascular conditions. It is an unrestrained progression of cells followed by deterioration of tissues or organs. There are quite a few types of cancers, varying on the organ of their origin. Chemotherapy, radiotherapy, resection and immunotherapy are practiced for the cancer treatment. The drawback associated with persistent chemotherapy is the advancement of drug resistance by the tumor cells. It has been suggested that combinational therapy practices can avoid drug resistance and can be more efficient in cancer treatment. Technical advancements in the progression of DDS have hugely transformed the conventional practices of medication. This advancement would never have been possible without the uncompromising study in the area of biomaterials across the world (He *et al.*, 2020; Senapati *et al.*, 2018). It would be pertinent to mention a historical sketch of the biomaterial applications. Though the derivation of the word 'Biomaterial' cannot be traced very precisely, yet the developments with time can be outlined. The history of biomaterial applications can be drawn back to more than 2000 years ago where gold was generally utilized for dental ailments by Chinese and Romans. In the early twentieth century, the developments in biomaterials got accelerated due to the dawn of synthetic plastics. Much of the progress was seen during World War II. The Society of Biomaterials was formed in 1975 after a chain of symposia in the 1960s and 1970s (Huebsch and Mooney, 2009). It will be no hype that current fields like Drug delivery, Biosensors, Tissue Engineering and Theronastics owe a lot to biomaterials. Roughly, a biomaterial can be defined as a material that is non-toxic, biocompatible and does not elicit any unpropitious immune response when it encounters the living tissues. It has been said that the concept of biocompatibility becomes the central dogma of the biomaterials. Biocompatibility is the "ability of a material to perform with an appropriate host response in a specific application" as defined in David Williams Dictionary of Biomaterials. Biocompatibility is an intricate process, and it depends on numerous factors. It is a safety evaluation, and it labels the identification of suitable host response against the contact with biomaterial-based device or system (Ghasemi-Mobarakeh *et al.*, 2019). It relates the assets of biomaterial with the specific area of application. It accesses the time duration for the start of an immune rejection. The idea of biomaterial devices gets beaten if it begins an unfavorable immune response, which will eventually commence to the refusal of the device by the body. Much of the scientific research on biomaterial-based systems endeavor on improvement in the properties of materials to minimize the improper response in-vivo (Anderson, 2019).

Biomaterials are broadly classified as Natural, Synthetic and Semi-synthetic materials. A considerable amount of development in the biomaterial evolution involves polymers as significant players. Natural polymers obtained from bacteria, weeds, plants, and other living organisms are biocompatible in nature, less toxic, and biodegradable. It is said that the inadequate mechanical strength of natural polymers limits their widespread applications. These natural polymers are nowadays chemically modified to expand the mechanical durability and for the integration of the desired property. Extra functionalities are being affixed to the original polymer chains to meet the clinical needs, high drug loading capacity and controlled release (Mohan *et al.*, 2016). Such alterations require meticulous monitoring for maintaining the balance between the changes of the properties with no increase in toxicity. Another approach involves the crosslinking of two different polymers for accomplishing desired assets. Crosslinkers interconnect the molecules between the different polymeric chains. This practice was suggested as a result of inefficient attributes of individual polymers. Although the crosslinking might increase the weight of the polymer blends and provide them with enhanced stability, it might affect the degradation quality with a tangible addition in toxicity (Mogoşanu *et al.*, 2016). Composites are the systems engineered with two or more discontinuous phases having a significant difference in chemical and physical properties. The compositional entities are usually immiscible and separate at the macroscopic level. The constituents of a

composite structure are roughly categorized into two units known as continuous phase (Matrix) and discontinuous phase (dispersed phase, fillers, reinforcing agent) (Mogoşanu *et al.*, 2016). The continuous phase occupies the notable volume of the composite material providing a favorable environment for other dispersed phases to maintain their integrity and position. The matrix provides the fundamental structure for the other constituents. Composites can be either homogenous (equal spreading of the dispersed phase throughout the matrix) or heterogeneous (with unequal distribution of dispersed phase) (Matthews and Rawlings, 1999; Wang, 2003).

Biocomposites are the composite systems built up of biodegradable polymers for extensive biological applications. The fundamental guiding force after the growth of biocomposites is to accomplish the required strength, desired transport mechanism, flexible erodible properties, and biocompatibility. Natural polymers, as well as synthetic polymers, are engaged in the fabrication of biocomposites widely explored for their applicability in tissue engineering and drug delivery. Another benefit of biocomposites is the synergism of its constituents to produce unique properties in the composite. The characteristics of biocomposites can be altered by controlling the features like the number of dispersed phases, dispersion phase, and the quantity of each dispersed phase and varied processing methods. Chiefly the higher reinforcement presents with high strength to the composite. Strength depends a lot on the grip between the phases governing the tensile strength. Different polymeric chains interact in the form of various bonds ranging from weak hydrogen bonds and van der Waal forces to high strength covalent bonds (Gurunathan *et al.*, 2015). The hydrophilic and the hydrophobic chain arrangements govern the steadiness of the composite structure. Bionanocomposites are the biocompatible and biodegradable nanostructured composites. They earned much value in the last decade with the advancements in the field of drug delivery (Mokhtarzadeh *et al.*, 2016). The present article focuses on the biocomposite polymers for drug delivery in cancer. It highlights their physicochemical properties, classifications of the polymers, development methods and wide applications of biocomposite polymer matrix based drug delivery various cancer types.

Classification of Biopolymers Exploited in Matrix Development

Biopolymers used for composite matrices to formulate DDS are broadly classified as Natural and Synthetic polymers.

Natural Polymers

Natural polymers are acquired from a broad spectrum of plants, animals, and microbes. They are formed during the organism's life as an elemental part and are biodegradable. The sophisticated metabolic machinery of cells carries out the chain reactions required for the maturity of a polymer from the monomer substrates. These polymers can be linear or branched, comprising hundreds to thousands of basic monomeric units. Natural polymers can have their fundamental structures in the form of carbohydrates, proteins and lichens. Microbes all over nature are found occurring inside the biofilms, which are exopolysaccharide chains made up of monosaccharides or disaccharide monomers (Rehm, 2010; Kenar *et al.*, 2019). The microbial population is the source of a large group of endopolymers and exopolymers. Terrestrial as well as aquatic flora and fauna are the source of a comprehensive range of carbohydrate and proteinaceous polymers. Owing to the natural origin of such polymers, seasons and species of an organism determine their attributes. Natural polymers are the primary metabolic components of such organisms, and they demand to be extracted for their wide applications. These polymers have many advantages, including their low prices, broad availability, non-toxic nature and biodegradability. However, they are poor at mechanical or tensile strengths and thermal properties (Verma *et al.*, 2019; Jain and Jain, 2015; Jain *et al.*, 2013; Tiwari *et al.*, 2019; Subudhi *et al.*, 2015; Bishnoi *et al.*, 2020; Prajapati *et al.*, 2019a; Kumari *et al.*, 2018; Jain *et al.*, 2018a,b; Verma *et al.*, 2018). **Fig. 1** depicts the origin-based classification of polymers.

Synthetic Polymers

After Natural polymers, there was a resurgence in the exploitation of synthetic polymers for biological applications. To date, they have been explored for, drug delivery, controlled release capsules, bio-packaging, tissue regeneration and implants. The most commonly studied polymers include PEG, PLA, PLGA, PMMA, and PCL (Bastioli, 2020; Jain *et al.*, 2020; Kumari *et al.*, 2018, 2016). A broad spectrum of investigations across the globe has been reported for these synthetic polymers. They provide better tensile strength and are often looked upon for the improvement of mechanical and thermal strength. From drug delivery point of view, PEG is the most exploited polymer ranging from low molecular weight chains to high molecular weight chains and from pure PEG chains to its derivatives (Saraf *et al.*, 2020a; Jain *et al.*, 2019a; Jain and Jain, 2018, 2017, 2016b; Saraf *et al.*, 2016; Jain and Jain, 2016a; Jain and Sanjay, 2016; Jain and Jain, 2016c). **Table 1** summarizes exploited polymers for the development of the biopolymer matrix.

Desired Physicochemical Properties of Biopolymers for Composite Development

Biopolymers are exploited for their unique properties while the development of composite matrices. Each composite is formulated to achieve desired characteristics by the perfect blend of unique attributes possessed by its constituting polymers (Masuelli and Renard, 2017). These polymers have several characters elaborated as follows.

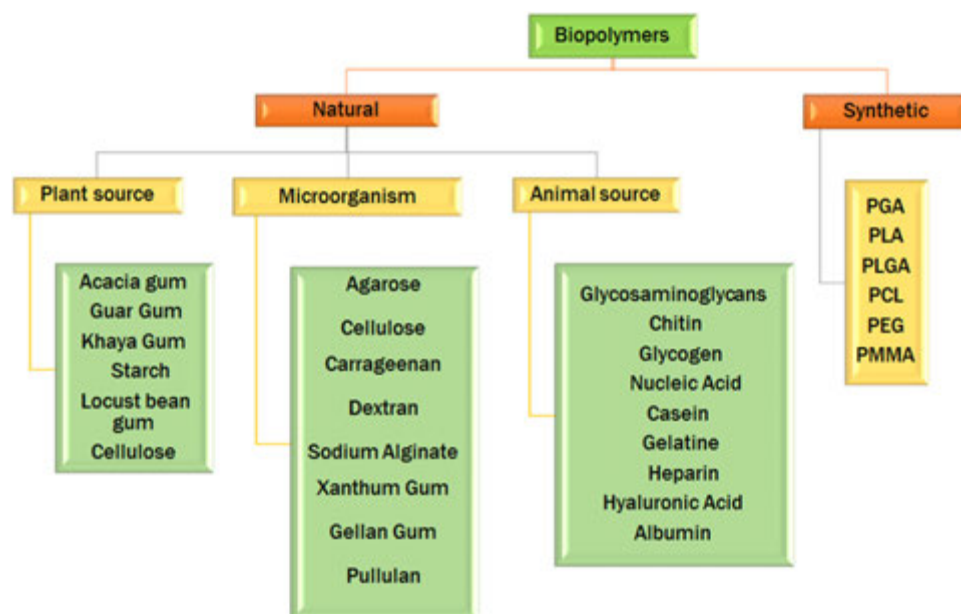


Fig. 1 Origin-based classification of polymers.

Biocompatibility

The biopolymer composites should be biocompatible and it is determined by its applicability. The factors which influence the biocompatibility of biopolymer-based systems include material contact with the surroundings, duration of the interaction, functional characteristics, surface, and architectural compatibility. Alginate gained a lot of weight by the virtue of its attributes and extensive application possibilities in biomedical fields. Biocompatibility studies have been reported for alginate and alginate-blends. They present an array of in-vitro assays for the estimation of the biocompatibility related to alginate formulations (Spasojevic *et al.*, 2014; Dhalendra *et al.*, 2020). Oral administration of alginate is believed to be safe by the FDA. Spasojevic *et al.* reported the immune responses due to the paucity of proper purification of alginate during extraction (Spasojevic *et al.*, 2014). Similarly, Albumin is a readily found plasma protein in animals that has been extensively accepted for the development of DDS. Albumin and albumin-based formulations have been examined for their toxic responses. Most of the investigations point towards the biocompatible nature of the albumin formulations. Abraxane was the first Albumin-Paclitaxel system which got accepted by the FDA for the cancer chemotherapy. Similar to alginate, chitosan is a much desired polymer, and it is one of the most used polymers as well. It is generally utilized for the matrix formulations. The majority of the findings assume it to be non-toxic established on its FDA approval for wound dressings. This approach is erroneous if we talk about nanoparticles, microparticles or other regenerative applications. Chitosan is a positively charged polymer which interacts with the negatively charged membranes of our cells (Rodrigues *et al.*, 2012). A proper nexus of protocols should be followed while assessing the biocompatibility of chitosan. Other polymers like gellan gum, carrageenan, dextran, hyaluronic acid agarose, PEG and PLGA are being looked upon for a number of applications. The toxicity studies have been performed for their in-vitro and in-vivo usage (Lim *et al.*, 2010; Cadée *et al.*, 2000; Liu *et al.*, 2017; Da Silva *et al.*, 2018; Cai *et al.*, 2018).

Mucoadhesiveness

Mucoadhesion can be described as the attractive force between the biological material and the mucus layer. There are numerous theories to elucidate the adhesive mechanisms. This adhesion is mostly hydrophilic interactions and hydrogen bonding. It is of absolute value to appreciate these hydrophilic bonding while formulating efficient films for application. Oro-mucosal DDSs is advantageous over the conventional oral drug delivery as it can easily escape the acidic atmosphere of the stomach, intestinal enzymes and the first-pass metabolism. Though it is advantageous over conventional oral drug delivery, there are challenges in their efficient development and functioning (Brandl and Bauer-Brandl, 2019). The lag in the initiation of a proper adhesion between the mucosal layer and the delivery system paves limitations. Hydroxypropyl methylcellulose and sodium alginate have been broadly explored for their mucoadhesive properties. The usage of biopolymer matrices has made a considerable contribution to the sublingual delivery as well (Ammar *et al.*, 2017). Synthetic polymers and clay provide the mechanical and thermal properties to the biocomposite matrices. Trastullo *et al.* reported higher drug penetration from the polymer blends of HPMC gelatine, chitosan and sodium hyaluronate. Another challenging field is of ophthalmic drug delivery. The liquid drops used for correcting eye ailments are not absorbed well, and there is a demand for more efficient ways (Liu *et al.*, 2016b). Bionanocomposite nanoparticles are now being developed for sustained ophthalmic delivery of drugs.

Table 1 Exploited polymers for the development of the biopolymer matrix

<i>Natural Polymers</i>				
<i>Polymer</i>	<i>Source</i>	<i>Composition</i>	<i>Application</i>	<i>Reference</i>
Hyaluronic acid	All vertebrates	D-glucuronic acid and <i>N</i> -acetyl-D-glucosamine	Spinal cord injury, bone and cartilage repair, drug delivery, cancer-targeting moiety	(Prajapati <i>et al.</i> , 2020b, Prajapati <i>et al.</i> , 2019b, Pulakkat <i>et al.</i> , 2016)
Chitosan	Animal exoskeletons and shells	D-glucosamine and <i>N</i> -acetyl-D-glucosamine	Wound healing, orthopedics, cardiac repair, neural tissue engineering, cornea repair, drug and gene delivery	(Jain and Jain, 2013, Wang <i>et al.</i> , 2020)
Carrageenan	<i>Chondrus crispus</i> seaweed	Galactose and Anhydrogalactose	Skeletal tissues regeneration, cell delivery system	(Rode <i>et al.</i> , 2018)
Agarose	Red weed	D-galactose and 3,6-anhydro-L-galactopyranose	tissues regeneration, cartilage substitutes nerve regeneration, cancer drug delivery	(Zarrintaj <i>et al.</i> , 2018)
Gelatine	Animal skin and bones	Ala-Gly-Pro-Arg-Gly-Glu – 4Hyp-Gly-Pro	Wound healing, drug delivery, soft tissue engineering, cell delivery, and in vitro stem cell maintenance	(Yang <i>et al.</i> , 2018)
Fibronectin	Produced in animal liver	Polypeptide chains; Protein dimer	Wound healing, stem cell differentiation, cardiac repair, bone regeneration	(Casanova <i>et al.</i> , 2020)
Albumin	Present in animals	60–70 kDa protein	Drug carrier, bioprinting, tissue regeneration, cancer drug delivery	(Zhang <i>et al.</i> , 2020a)
Starch	Derived from plants	Homo-glucose polymer	Binding agent, drug delivery	(Torres and Troncoso, 2020)
Alginate	Brown algae	(1–4)-linked β -D-mannuronate (M) and its α -L-guluronate	Bioprinting, Drug delivery, stem cell differentiation, cancer drug delivery	(Jain and Bar-Shalom, 2014, Soltan <i>et al.</i> , 2019, Jain <i>et al.</i> , 2018a)
<i>Synthetic Polymers</i>				
PLA	Polyester of two monomers: Lactic acid and cyclic di-ester lactide	3D-printing, bioprinting, biodegradable medical devices, tissue engineering, drug delivery	(Gregor <i>et al.</i> , 2017)	
PLGA	Poly(lactic-co-glycolic acid)	Biomedical devices, drug carriers, 3D-bioprinting, Hydrogels	(Zhang <i>et al.</i> , 2017, Zhang <i>et al.</i> , 2020b)	
PCL	Poly caprolactone Ring opening polymerization of ϵ -caprolactone	Implants, medical devices, drug delivery, tissue engineering	(Arunraj <i>et al.</i> , 2013)	
PEG	Poly ethylene oxide - H – (O – CH ₂ – CH ₂) _n – OH	Spinal cord injury, drug delivery, Tissue engineering, laxatives, cosmetics	(Kondiah <i>et al.</i> , 2020)	
PAA	Poly Acrylic Acid Homo-polymers of acrylic acid	Hydrogels, orthopedic implants, tissue engineering, cosmetics	(Chuah <i>et al.</i> , 2018)	
PMMA	Poly(methyl-Methacrylic acid)	Bone implants, lenses, bone cement, drug delivery	(Chen <i>et al.</i> , 2018)	

Gel-Forming Ability

Natural biopolymers usually possess hydrophilic character and gel-forming attributes. In water, they form a cross-linked mesh and can be utilized to embed the active molecules inside them. These gels are often referred to as hydrogel. A hydrogel can change its structure accompanied by the change in volume upon getting an appropriate stimulus like temperature or pH change. They are being explored for their tissue regeneration property in ailments such as spinal cord regeneration, rheumatoid arthritis, soft tissue ailments etc. (Ahmed, 2015; Li and Mooney, 2016). These hydrogels hold the feature to provide an appropriate framework for the cells and tissues to grow. Alginate and chitosan are the polymers of choice for the hydrogel formulations. Other polymers such as cellulose, gelatin, hyaluronic acid, collagen and PEG are also used for hydrogel developments for several applications. Injectable hydrogels are now being worked upon for better patient compliance and to ease the complication of targeted delivery of drugs (Narayanaswamy and Torchilin, 2019).

Principal Targeting Approaches for Drug Delivery to Cancer

Passive Targeting

In this, the macromolecules including nanocarriers consolidate especially in the cancerous tissues due to a mechanism of enhanced permeability and retention (EPR). In some conditions, the endothelium blood vessels become leakier than in the normal condition. In the case of hypoxia, the speedily growing tumor admits newer vessels or engulfs pre-existing vessels. Basically, the penetration of

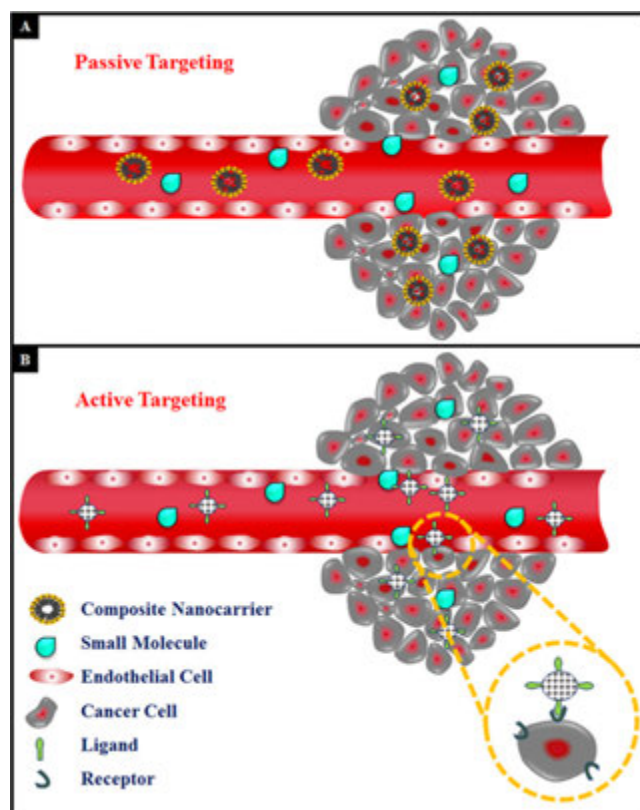


Fig. 2 Principal targeting approaches of drug delivery to cancer (A) Passive targeting and (B) Active targeting.

particles/macromolecule or carrier system depends on the size, impaired lymphatic drainage and leaky vasculature and. The carrier system or macromolecules enters through the capillaries of leaky tumor or by passive diffusion mechanism. The low molecular weight compounds enter by the diffusion (**Fig. 2(A)**). Convection via the tumor interstitium is deprived owing to interstitial hypertension, excluding diffusion as the leading discipline of drug transport ([Bertrand et al., 2014](#)). The EPR phenomenon plays a key role while designing the drug carrier system for cancer-targeting. Furthermore, for approximately all rapidly developing solid tumors the EPR effect is appropriate. Literally, it can be seen in all types of cancer except the hypovascular tumors (prostate or pancreatic cancer) ([Maeda et al., 2001, 2009](#); [Shukla et al., 2019](#); [Panda et al., 2019](#)). Some characteristics are especially important for these purposes are (1) the macromolecule or carrier should be anionic or neutral to circumvent the renal elimination; (2) nanocarriers should be stealthy from reticuloendothelial system to avoid their relapse via opsonization subsequent to phagocytosis. The size should be near to 10–100 nm to avert them from the evasion of kidney filtration. The size should exceed 10 nm and it must be smaller than 100 nm to prevent their stockpiling in the liver ([Gullotti and Yeo, 2009](#); [Nie, 2010](#)). Though, the EPR effect offers somewhat modest tumor exclusivity with 20%–30% in delivery rises than normal organs. The influence of EPR highly depends on the tumor biology and in particular: (1) the extent of perivascular tumor growth and the density of the stromal response, (2) the extent of lymphangiogenesis and angiogenesis, (3) intratumor pressure ([Arap et al., 1998](#)). It is likely to modify the EPR effect mechanically or chemically to attain vascular normalization to highly accretion of nanosystems. Some examples of chemical enhancers of EPR are prostaglandins, peroxynitrite, nitric oxide, bradykinin (kinin), vascular permeability factor /vascular endothelial growth factor and other cytokines, the use of such enhancers momentarily extend tumor perfusion ([Attia et al., 2019](#)).

Active Targeting

The active targeting is imperative to deliver the drugs, theranostics, or gene to the desired site averts their entry to normal tissues and so boosts the therapeutic competence and limits the side effects. This mechanism markedly enhances the concentration of drug at the target site than the passively targeted system or free drug. Generally, it is also termed as ligand-mediated targeting because various kinds of the ligand can be linked to the surface of the carrier system through which these are captured by the receptors of the targeted cells (**Fig. 2(B)**). This perspective is intended to augment the interaction between the cells and the carrier system to increase the entry without varying the biodistribution. For active targeting, the receptors on the desired cells should be expressed unvaryingly. Ligands may be monoclonal antibodies (mAbs), antibody fragments or non-antibody. The binding capacity of the ligands affects penetration because of the “binding-site barrier” ([Adams et al., 2001](#); [Saraf et al., 2020b](#)). The increased cellular internalization is responsible for the anti-cancer potential of nanocarriers by active targeting rather than enhanced tumor accumulation. Ligand anchored nanocarriers

result in direct cell kill, along with cytotoxicity to the cells of cells that are at the tumor periphery and are independent of the tumor vasculature. The transferrin receptors are approximately 100 folds more overexpresses than in the normal cells. Its extracellular accessibility, potential to internalize and chief role in the cellular pathology of cancer make transferrin receptor a fascinating target. Some other receptors such as folate, epidermal growth factor receptor (EGFR) and glycoprotein receptor are also present on cancerous cells (Danhier *et al.*, 2010; Attia *et al.*, 2019; Jain *et al.*, 2019b).

Stimuli-Responsive Delivery

Nanocarriers can uphold stealth function throughout the movement, upon reaching the tumor site. The conversion of the nanocarriers is prompted by the exceptional tumoral extracellular environment, either by internal stimuli (pH, redox, and enzyme) or by external stimuli (light, mechanical force, electric field, Photothermal, and magnetic field) permitting the release of the drug or the involvement with a particular target. The external stimuli can help to retain drugs within the nanocarrier and for the controlled release of the drug. Such types of smart delivery systems have a variety of applications in the field of biology, medicine, drug delivery, and biosensors. Various research studies have carried out on stimuli-responsive biopolymer composite for drug delivery. Such smart biopolymer matrix can be utilized in biological, medicinal, drug delivery and biosensing applications. Such intelligent polymers have found many applications in the fields of biology and medicine and can be used as sensors and biosensors for controlled and triggered drug delivery (Hu and Liu, 2010; Bajpai *et al.*, 2008; Jain *et al.*, 2018c; Prajapati *et al.*, 2020a). The design of the biopolymer matrix must ideally be easy to administer, should be capable to deliver the drug at the desired target site and the blend of the polymer should be biocompatible and non-toxic (Wei *et al.*, 2017).

Overview of Development Methods

The biopolymer matrix composite comprises the properties of two or more polymeric material to attain better physicochemical and biological properties while delivering the drug. Biopolymer-based composites have been developed by the use of various tactics. Out of them, some widely used methods are solvent casting (Park *et al.*, 2017), phase separation (Shao *et al.*, 2012), electrospinning (Bianco *et al.*, 2009; Ghosal *et al.*, 2018) and freeze-drying (Hottot *et al.*, 2004; Fig. 3). A detailed account of these methods is provided in Table 2.

Role of Exploited Biopolymers in Matrix Development

Biodegradable polymeric composites can achieve anti-cancer targeting via various mechanisms. This comprises delivery to the tumor cells enabled by extended circulation in the blood, capacity to enable transport across the endothelium to the tumor, and ligand-mediated targeting. Targeting tumor vasculature is a prime target as the tumor-associated neovasculature is a key to permitting the tumor to obtain enough oxygen and nutrients to allow growth. Besides, their biodegradability, biocompatibility, and non-immunogenicity make them a material of choice for anticancer drug delivery. Different types of biopolymers such as hyaluronic acid, chitosan, polylactic acid, and polylactic acid-co-glycolic acid, etc. are well reported for anticancer drug delivery (Prajapati *et al.*, 2019; Gulbake *et al.*, 2017).

Drug Delivery Applications of Biopolymer Matrix in Various Cancers

Breast Cancer

Bano *et al.* (2016) reported the promising result of chitosan (CS), bovine serum albumin (BSA), or carboxymethyl cellulose (CMC) and then coated with NiFe_2O_4 . The activity of composite was evaluated on the MCF breast cancer cell line. The outcomes of the study revealed that composite delivers a single combinatorial tactic to expand the biocompatibility and improve the relaxivity value. The outcomes powerfully reinforced the ability of BSA, CS and CMC composite to cancer cells. The prepared system i.e., BSA@NFs, CS@NFs and CMC@NFs can potentially be used as imaging probes while targeting MCF-7 cancerous cells. Song *et al.* (2018) fabricated the magnetic chitosan/alginate nanoparticle loaded with curcumin. A sustained release of drug was observed. Confocal fluorescence microscopy (CLSM) data revealed site-specific delivery of curcumin by applying the magnetic field. The cell sorting assay revealed that nanoparticles showed significant uptake capacity than free curcumin to the MDA-MB-231 cells. MTT assay revealed its potential cytotoxic effect on the MDA-MB-231 cells compared to HDF cells (Song *et al.*, 2018). In research, Bhunchu *et al.* (2016) for the delivery of curcumin diethyl disuccinate (CDD), worked to prepare chitosan/alginate composite nanoparticle CDD loaded chitosan/alginate nanoparticle depicted excessive toxicity toward breast adenocarcinoma cells (MDA-MB-231) (Bhunchu *et al.*, 2016). Chitosan/alginate composite nanoparticles were developed by Rahaiee *et al.* (2017) for the delivery of crocin. The cell viability evaluated on MCF-7 cells, the cell viability found to be decreased as the concentration of crocin increased. Though, a higher (10 mg/mL) dose of crocin caused tissue necrosis. Noticeable difference in cell mortality observed

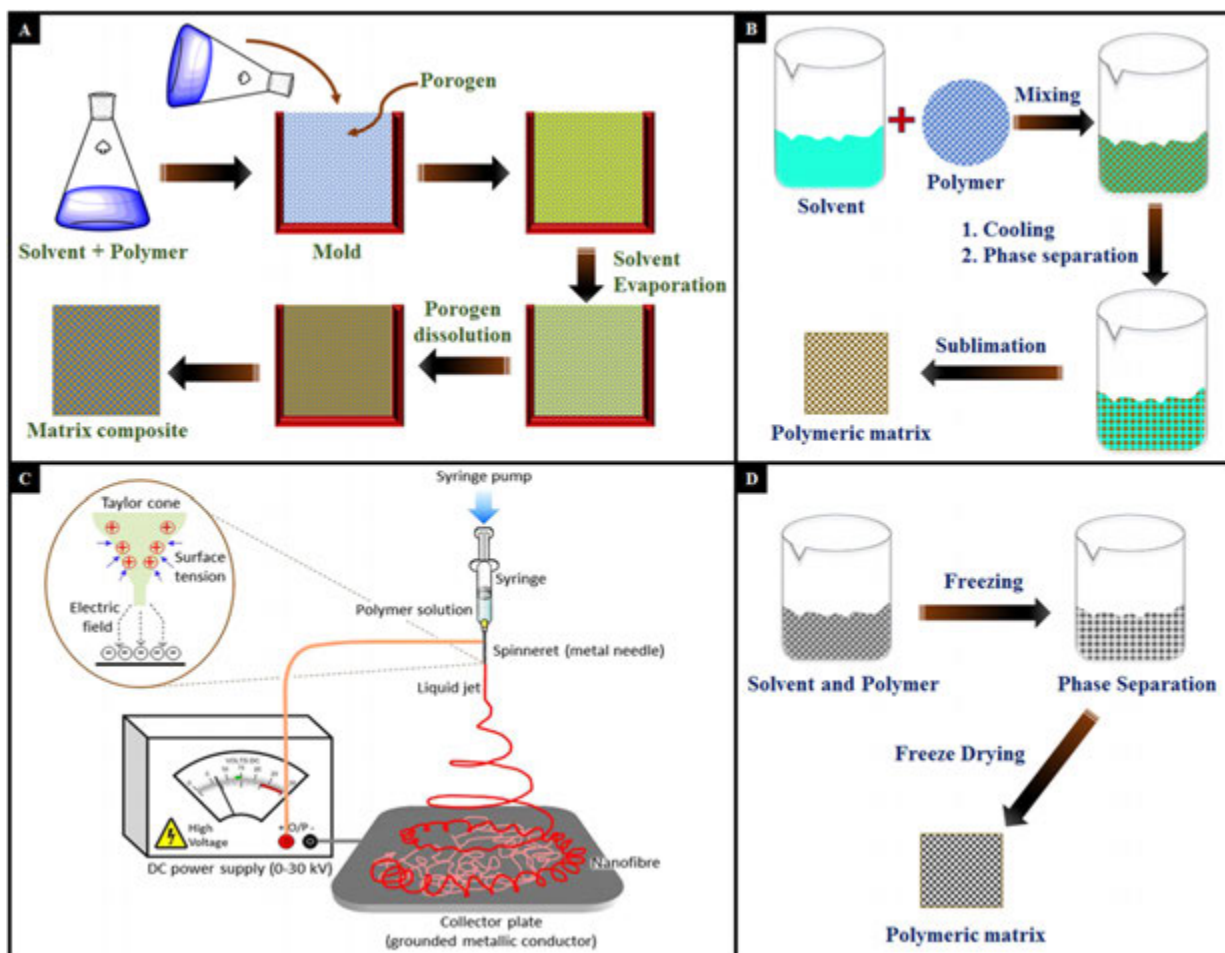


Fig. 3 Overview of development methods: (A) Solvent Casting, (B) Phase Separation, (C) Electrospinning, and (D) Freeze Drying. (C) Reprinted with permission from Ghosal, K., Chandra, A., Praveen, G., et al., 2018. Electrospinning over solvent casting: Tuning of mechanical properties of membranes. *Scientific Reports* 8, 1–9.

Table 2 Methods of biopolymer matrix composite development

Method	Remark	Reference
Solvent casting	- The solvent casting method is based on the dispersal of a porogen in a liquid or powder-based stuff. - The polymer solution is hardened either by solvent evaporation or cross-linking. - The powder is compacted using pressure and temperature. Porogen particles are then melted in a specific solvent, and then the structure is generated.	(Park <i>et al.</i> , 2017)
Phase separation	- In this method, the thermodynamic demixing of the polymer solution into the polymer-rich phase and polymer poor phase occurs at the time of cooling. - Further, polymer affluent phase solidifies, and polymer poor phase is removed. Sublimation was done to remove the solvent.	(Shao <i>et al.</i> , 2012)
Electrospinning	- Electrospinning is an economic technique. - It is governed by an electric field of high magnitude between electrodes, which are located in a polymer solution, and a collector with electric charges of opposite polarity. - The polymer solution pulled from a nozzle under gravity or by mechanical pressure united with an electric field (5–50 kV). - A polymer jet is produced as the surface tension of polymer droplet increases due to the electric field. - Then the solvent evaporated, resulting in the formation of solid nanofibers.	(Bianco <i>et al.</i> , 2009)
Freeze drying	- The freeze-drying tactic is applied at low temperatures, which is helpful for integrating heat-sensitive bioactive molecules in the polymer composite. - In this technique, the formation of ice crystals leads to the induction of porosity via sublimation and desorption. - This method comprises a dispersed water phase and a continuous organic phase having biodegradable polymer which will then produce the composite. - At the time of freezing, the solution of the polymer is chilled. - Subsequently, the solvent's ice crystal forms, therefore compelling polymer molecules to aggregate in interstitial spaces. - Then, to remove the solvent the pressure is applied which will lower than the equilibrium vapor pressure. - The sublimation of the solvent produces the dry polymer composite.	(Hottot <i>et al.</i> , 2004)

between blank and drug-loaded nanoparticles. The cell viability of MCF-7 cells was found to be concentration-dependent (Rahaiee *et al.*, 2017). Qin *et al.* (2018) prepared paclitaxel and epirubicin loaded mPEG-g-CS coated PLGA NPs. No effect on the cell viability of MCF-7 cell and HUVEC (human umbilical vein endothelial cells) were seen in the case of blank nanoparticles. A significant reduction in cell viability was seen might be due to an increase in drug concentration. In comparison to free drug, the viability of both the cell line when treated with core shell nanoparticles found to be reduced confirming the potential of drug-loaded nanoparticles. Both the drugs when used together showed a synergistic effect. The maximum cytotoxicity of core-shell nanoparticles can be accredited to the greater anti-tumor's consequence of the mutual chemotherapy when compared with a single drug (Fig. 4; Qin *et al.*, 2018).

Colon Cancer

Hung *et al.* (2019) developed AuNPs/biopolymer composite to deliver doxorubicin (DOX) to the colon. AuPPPyA and AuPPPyB two composite with different drug loads were developed. The rate of tumor inhibition was near 46.2% and 66.4% respectively for AuPPPyA and AuPPPyB which was significantly higher than DOX alone (30%). MTT assay confirmed that DOX-AuPPPyA and DOX-AuPPPyB showed more cytotoxicity to the DLD-1 and HCT-116 colorectal cancer than free DOX confirming their potential for colon cancer treatment (Hung *et al.*, 2019). Sun *et al.* developed nanocomposite beads by the use ZnO/carboxymethyl cellulose/chitosan. 5-FU loaded to these beads showed sustained release of drug in colonic simulated fluid which was dependent on the concentration of composite material (Sun *et al.*, 2019a). In another study, alginate/chitosan/kappa-carrageenan (Alg/Cs/kC) composite microbeads loaded with 5-fluorouracil (5-FU) were developed by Sun *et al.* (2019b) 5-FU release was found to be lessened by adding supplementary kC layer from 14% to 7% in the dual-layered Alg/Cs/kC microbeads. Moreover, the release markedly enhanced under simulated intestinal and colon environments. Rajan *et al.* (2013) prepared nanocomposite by combining chitosan-PEG-gelatin polymer for delivery of 5-FU. The cytotoxicity was assessed on the colon cancer cell line (COLO-205 and HT-29). The developed nanosystem was found to be less cytotoxic compared to the 5-FU after incubation for 3–12 hrs. No significant variances were seen between the negative control and unloaded nanoparticles after incubation for 24. The cytotoxicity of the carrier system was reliant on the concentration of the drug (Rajan *et al.*, 2013). Guar gum modified stimuli-responsive nanocomposite for colorectal cancer treatment was developed by Kumar *et al.* (2019). The study described a strong green-emitting core-shell photoluminescent upconversion nanocrystals (CSGU) designed to synergistically accomplish stimuli-responsive i.e., enzyme and photodynamic prompted delivery of the drug for boosted therapeutic consequences on HT-29 colon carcinoma cells in vitro (Kumar *et al.*, 2019).

Lung Cancer

Zhang *et al.* (2019) prepared the hyaluronic acid/ chitosan nanoparticles for the delivery of siRNA to the lung cancer cells. The results exhibited efficient delivery of siRNA to A549 cells and repressed cell proliferation by downregulating the target gene BCL2. In vivo data exposed that the nanoparticles delivered a significant concentration of siRNA to the tumor, ensuring the inhibition of tumor growth (Zhang *et al.*, 2019). Arya and Katti (2015) prepared the composite particle of paclitaxel and topotecan loaded Poly (d, l-lactide-co-glycolide)-chitosan and evaluated their potential for NCI-H460 lung cancer cell line. Drug loaded composite particles revealed improved cell death of NCI-H460 tumoroids then the additive effect of paclitaxel and topotecan when compared individually (Arya and Katti, 2015). Baspinar *et al.* (2019) prepared paclitaxel loaded zein nanoparticles with or without the use of chitosan. The efficacy was evaluated on the A549 lung cancer cell line. The cytotoxicity exposed that 10 nM concentration of PTX concentration was enough to reduce the viability of cells to 35% in the case of nanoparticles without chitosan and 25% in the case of nanoparticles with chitosan. The maximum concentration (50 nM) was found to decrease the viability to 15% and 20% in the case of nanoparticles without chitosan and in the case of nanoparticles with chitosan, respectively (Baspinar *et al.*, 2019).

Cervical Cancer

Das *et al.* (2010) prepared composite nanoparticles from alginate (ALG), chitosan (CS), and pluronic for the delivery of curcumin. The cytotoxicity was evaluated on the HeLa cell line and at the concentration of 500 µg/mL nanoparticles found to be nontoxic (Fig. 5(A)). Curcumin showed concentration-dependent cell viability (Fig. 5(B)) and the projected half-maximal inhibitory concentration values for free and encapsulated curcumin was found to be 13.28 and 14.34 µM, respectively (Das *et al.*, 2010). Karimi *et al.* (2013) designed the nanoparticles of chitosan and albumin for the efficient delivery of genes. The cell viability potential was measured on the HeLa cell line. Alb-CS-DNA nanoparticles with 10 µg/mL concentration revealed 85% cell viability. The results were then compared with chitosan (Fig. 5). In the case of albumin cell viability 100% suggesting that albumin can promote biocompatibility. The cellular uptake study showed high Alb-CS-DNA nanoparticle by the cells (Karimi *et al.*, 2013).

Brain Cancer

Bazzazzadeh *et al.* (2020) for the delivery of temozolomide and paclitaxel developed poly(acrylic acid) grafted-chitosan/ polyurethane/ magnetic MIL-53 metal-organic framework composite. The cell viability Bax expression was evaluated on U-87 MG glioblastoma cancer cells. The results revealed that magnetic MIL-53 NMOFs loaded- PA-g-CS/PU/TMZPTX nanofibers can be effective for targeted anticancer

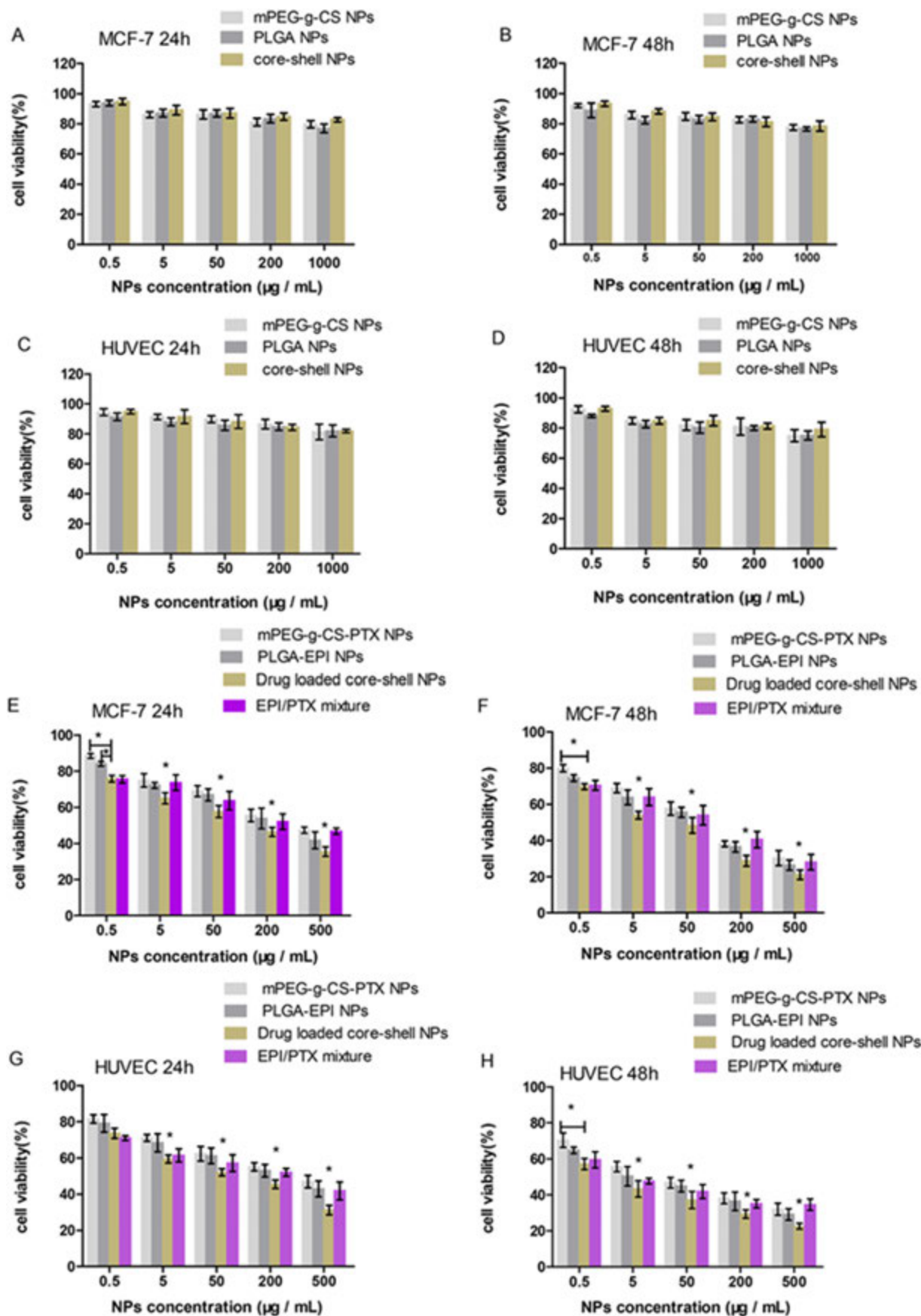


Fig. 4 Cell viabilities of NPs: (A–D) Effects of blank NPs on the viability and (E–H) Effects of drug loaded NPs on the viability of MCF-7 cells and HUVEC cells. Reprinted with the permission from Qin, J., Wei, X., Chen, H., *et al.*, 2018. mPEG-g-CS-modified PLGA nanoparticle carrier for the codelivery of paclitaxel and epirubicin for breast cancer synergistic therapy. *ACS Biomaterials Science & Engineering* 4, 1651–1660.

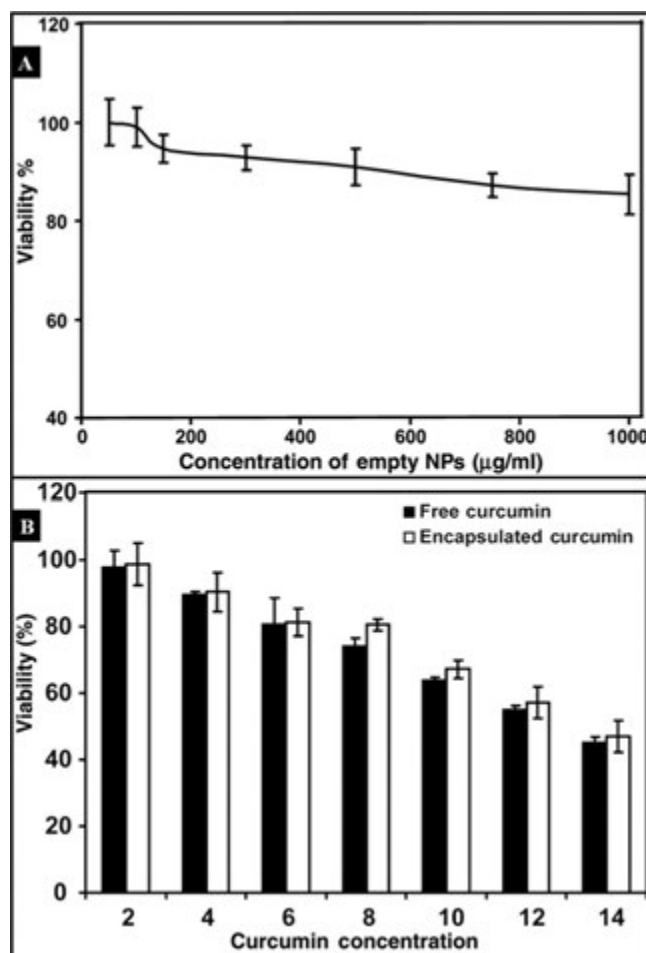


Fig. 5 Cytotoxicity assay: Cell viability of HeLa cells exposed to different concentrations of (A) blank ALG-CS-PF127 NPs and (B) free and encapsulated curcumin. Reprinted with permission from Karimi, M., Avci, P., Mobasseri, R., Hamblin, M.R., Naderi-Manesh, H., 2013. The novel albumin–chitosan core–shell nanoparticles for gene delivery: Preparation, optimization and cell uptake investigation. *Journal of Nanoparticle Research* 15, 1651.

drug delivery with apoptosis of 49.6% of U-87 MG glioblastoma cells (Bazzazzadeh *et al.*, 2020). Parmar *et al.* (2018) studied to develop polylactic acid co glycolic acid (PLGA) nanoparticles for the delivery of methotrexate (MTX) by conjugating transferrin. A biphasic drug release pattern was observed. Initially in 8hrs, > 35% drug release was observed and then sustained release (65%) by the end of 168 hrs. cellular uptake (quantitative) evaluation confirmed a collinear dependence on the concentration drug-conjugate. The tumor spheroid volume was significantly reduced when folic acid along with transferring conjugated on polysorbate 80 (P80) coated nanoparticles (P80-Mtx-Tf-FA-PNPs). The ex vivo cytotoxicity was evaluated on C6 glioma cell by SRB assay. P80-Mtx-Tf-FA-PNPs showed greater cellular cytotoxic effect when compared with another formulation group. At the concentration of 100 μM, the formulation incubated for 72 hrs resulted in 100% cell death of the cellular population. This might be attributed to the endocytosis by transferrin and folate receptor (Parmar *et al.*, 2018). Meenach *et al.* (2010) developed polyethylene glycol-based hydrogel nanocomposite for the hyperthermia. Magnetic PEGMMA/PEGDMA hydrogel nanocomposites can be effective in thermal cancer therapy via remote heating. Fig. 6 approves the potential of these experimentations, M059K glioma cells. The cells heated with hydrogel composite displayed discrete cell death at the center and an interface, while the favorable morphology was observed by the control group. On the other side, the IR images exhibited the final temperatures the cells were exposed to. Overall, these results show the ability of the gels to kill cancer cells without the magnetic field causing harm (Fig. 6; Meenach *et al.*, 2010).

Miscellaneous

Alemдар (2016) fabricated gelatin/alginate/hyaluronic acid composite film for the delivery of 5-FU. The cytotoxicity was evaluated on L929 fibroblast cells by WST-1 assay. No significant variation detected between the composite films w/out BA and control sample revealed that neat Gel/SA/HyA and Gel/SA/HyA/5 v. %BA did not cause a cytotoxic effect on the viability of L929 cells (Alemдар, 2016). Patiño-Ruiz *et al.* (2020) prepared chitosan/alginate nanodisk (Cs-Al nanodisks) and assessed their potential for prostate cancer. The Cs-Al nanodisks evaluated for cytotoxic effect on two different PWR-1E (human prostate cells line) and PC-3

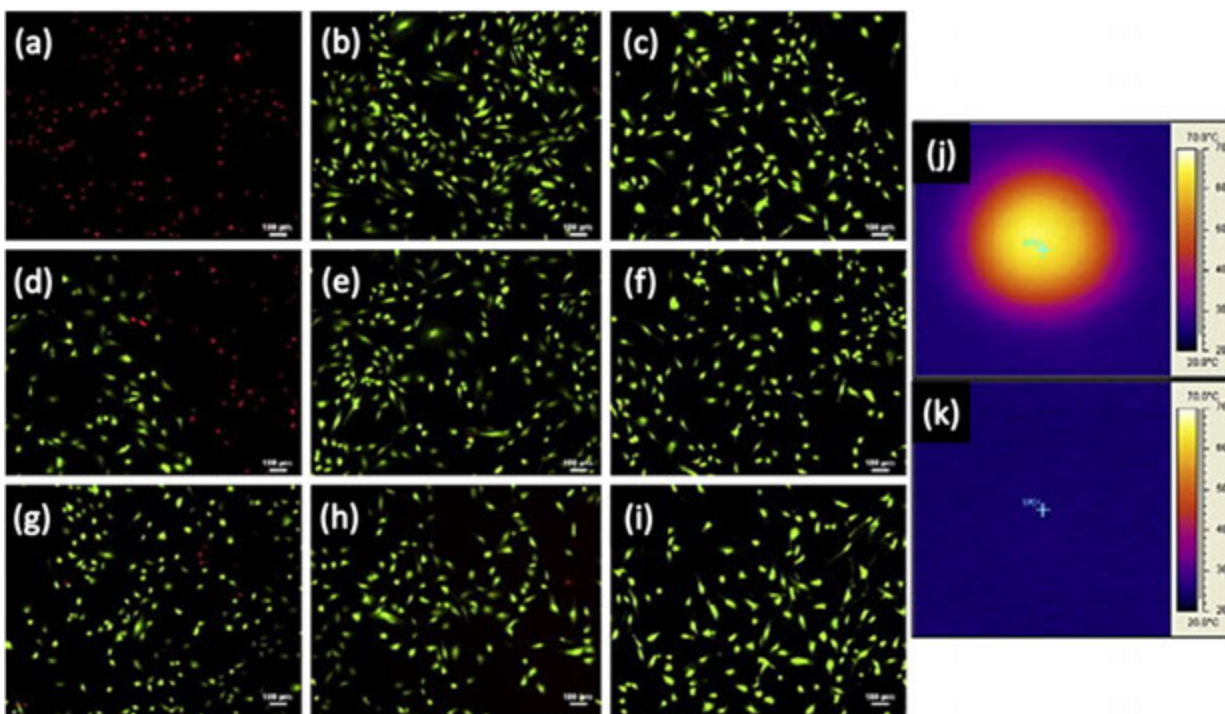


Fig. 6 M059K glioblastoma multiforme/hydrogel heating results: Images (a-i) represent fluorescent microscopy images after Live/Dead assay of M059K cells, where (a-b) are at the center of the Petri dish, (d-f) are at the interface between live and dead cells and (g-i) are at the outer edge, unaffected by heat. The first column of images are for cells exposed to a DM gel (50 mol.% PEG200MMA, 50 mol.% TEGDMA) at 297 kHz and 25 kA m⁻¹ for 5 min, the middle column is of cells exposed to an AMF only at 297 kHz and 25 kA m⁻¹ for 5 min and the right column is of cells not exposed to gels or an AMF. Images (j & k) represent IR images after the cells had been heated with the gel for 5 min (j) and exposed to an AMF for 5 min (k). Represented with the permission from Meenach, S.A., Hilt, J.Z., Anderson, K.W., 2010. Poly (ethylene glycol)-based magnetic hydrogel nanocomposites for hyperthermia cancer therapy. *Acta Biomaterialia* 6, 1039–1046.

(Caucasian prostate cell line). More than 80% of cell viability revealing low inhibition and defining the Cs-Al nanodisk as an optimistic technique for controlled delivery (Patiño-Ruiz *et al.*, 2020).

Conclusion and Future Scene

Biopolymers are material of choice for the purpose of anticancer drug delivery due to their distinguished properties than other materials. Biopolymers are biodegradable, biocompatible and non-toxic to the cells. Previously, blends of the biopolymers have been extensively used for tissue engineering, drug delivery and other medical applications. The blends prepared in the combination of the proper ratio can improve its mechanical strength for the fabrication of matrix composite. Improved biopolymers with distinct polymeric sections can affect properties altering their sensitivity, cellular uptake, and drug release. The functional groups existing on the surface of biopolymers can be exploited for crosslinking and bioconjugation with cell-targeting agents. The size is of great importance for organ or tissue-specific targeting. The decisive goal would be to exploit the diagnostic evidence and therapeutic efficacy, lessen the time for diagnosis, and decrease the extent and incidence of invasive interventions.

The selection of a biopolymer depends on the physicochemical properties of the drug and the characteristics of the tumor cells. The loading of the drug in the carrier system and their prevention is a challenging task. Most of the drug molecules get degraded in various enzymatic environments. Different types of combinations can help overcome such drawbacks. It is also challenging to define the proper concentration of the polymer to fabricate the polymer matrix of desired properties. In order to monitor compatibility with living tissue or a living system for its toxicity, injuriousness, or physiological reactivity without causing immunological rejection like antigenicity needs effective in vivo and clinical tests or efficient biological models mimicking the uptake of released drugs. Future advances in the execution of a biopolymer matrix in therapeutics would embrace the ability to scale-up without forfeiting the exact control. The development of effective approaches for harvesting biopolymer matrix along with ethical concerns need to be prioritized. Computational models need to be unified to clarify the effects on the degradation profile, intra- and extra-cellular trafficking of polymeric nanoparticles for increased commercialization. Computer-based optimization can be done to define the specific amount of polymers to achieve the desired properties of the polymer blend.

Acknowledgment

Dr. Ankit Jain acknowledges the financial assistance from the Department of Biotechnology (Govt. of India), Delhi in the form of DBT-RA (Postdoc).

Conflict of interest

The authors report no conflict of interest.

References

- Adams, G.P., Schier, R., Mccall, A.M., *et al.*, 2001. High affinity restricts the localization and tumor penetration of single-chain fv antibody molecules. *Cancer Research* 61, 4750–4755.
- Ahmed, E.M., 2015. Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research* 6, 105–121.
- Alemdar, N., 2016. Fabrication of a novel bone ash-reinforced gelatin/alginate/hyaluronic acid composite film for controlled drug delivery. *Carbohydrate Polymers* 151, 1019–1026.
- Ammar, H.O., Ghorab, M.M., Mahmoud, A.A., Shahin, H.I., 2017. Design and in vitro/in vivo evaluation of ultra-thin mucoadhesive buccal film containing fluticasone propionate. *AAPS PharmSciTech* 18, 93–103.
- Anderson, J.M., 2019. Biocompatibility and bioresponse to biomaterials. In *Principles of Regenerative Medicine*. Elsevier.
- Arap, W., Pasqualini, R., Ruoslahti, E., 1998. Cancer treatment by targeted drug delivery to tumor vasculature in a mouse model. *Science* 279, 377–380.
- Arunraj, T., Rejinold, N.S., Kumar, N.A. Jayakumar, R., 2013. Doxorubicin-chitin-poly (caprolactone) composite nanogel for drug delivery. *International Journal of Biological Macromolecules* 62, 35–43.
- Arya, N., Katti, D.S., 2015. Poly (d, l-lactide-co-glycolide)-chitosan composite particles for the treatment of lung cancer. *International Journal of Nanomedicine* 10, 2997.
- Attia, M.F., Anton, N., Wallyn, J., Omran, Z., Vandamme, T.F., 2019. An overview of active and passive targeting strategies to improve the nanocarriers efficiency to tumour sites. *Journal of Pharmacy and Pharmacology* 71, 1185–1198.
- Bajpai, A., Shukla, S.K., Bhanu, S., Kankane, S., 2008. Responsive polymers in controlled drug delivery. *Progress in Polymer Science* 33, 1088–1118.
- Bano, S., Zafar, T., Akhtar, S., *et al.*, 2016. Biopolymers coated superparamagnetic Nickel Ferrites: Enhanced biocompatibility and MR imaging probe for breast cancer. *Journal of Magnetism and Magnetic Materials* 1, 417 284–290.
- Baspinar, Y., Akbaba, H., Bayraktar, O., 2019. Encapsulation of paclitaxel in electrosprayed chitosan nanoparticles. *Marmara Pharmaceutical Journal*. 23.
- Bastoli, C., 2020. Handbook of Biodegradable Polymers. Walter de Gruyter GmbH & Co KG.
- Bazzazadeh, A., Dizaji, B.F., Kianinejad, N., Nouri, A., Irani, M., 2020. Fabrication of poly (acrylic acid) grafted-chitosan/polyurethane/magnetic MIL-53 metal organic framework composite core-shell nanofibers for co-delivery of temozolomide and paclitaxel against glioblastoma cancer cells. *International Journal of Pharmaceutics*. 119674.
- Bertrand, N., Wu, J., Xu, X., Kamaly, N., Farokhzad, O.C., 2014. Cancer nanotechnology: The impact of passive and active targeting in the era of modern cancer biology. *Advanced Drug Delivery Reviews* 66, 2–25.
- Bhunchu, S., Muangnoi, C., Rojsitthisak, P., 2016. Curcumin diethyl disuccinate encapsulated in chitosan/alginate nanoparticles for improvement of its in vitro cytotoxicity against MDA-MB-231 human breast cancer cells. *Die Pharmazie-An International Journal of Pharmaceutical Sciences* 71, 691–700.
- Bianco, A., Di Federico, E., Moscatelli, I., *et al.*, 2009. Electrospun poly (D-caprolactone)/Ca-deficient hydroxyapatite nanohybrids: microstructure, mechanical properties and cell response by murine embryonic stem cells. *Materials Science and Engineering C* 29, 2063–2071.
- Bishnoi, M., Jain, A., Singla, Y., Shrivastava, B., 2020. Sublingual delivery of chondroitin sulfate conjugated tapentadol loaded nanovesicles for the treatment of osteoarthritis. *Journal of Liposome Research*. 1–15.
- Brandl, M., Bauer-Brandl, A., 2019. Oromucosal drug delivery: Trends in in-vitro biopharmaceutical assessment of new chemical entities and formulations. *European Journal of Pharmaceutical Sciences* 128, 112–117.
- Cadée, J., Van Luyn, M., Brouwer, L., Plantinga, J., Van Wachem, P., *et al.* 2000. In vivo biocompatibility of dextran-based hydrogels. *Journal of Biomedical Materials Research: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and The Korean Society for Biomaterials* 50, 397–404.
- Cai, D., Fan, J., Wang, S., *et al.*, 2018. Primary biocompatibility tests of poly (lactide-co-glycolide)-(poly-L-orithine/fucoidan) core-shell nanocarriers. *Royal Society Open Science* 5, 180320.
- Casanova, M.R., Reis, R.L., Martins, A., Neves, N.M., 2020. Fibronectin Bound to a Fibrous Substrate Has Chondrogenic Induction Properties. *Biomacromolecules* 21, 1368–1378.
- Chen, S., Yang, J., Jia, Y.-G., Lu, B., Ren, L., 2018. A study of 3D-printable reinforced composite resin: PMMA modified with silver nanoparticles loaded cellulose nanocrystal. *Materials* 11, 2444.
- Chuah, C., Wang, J., Tavakoli, J. Tang, Y., 2018. Novel bacterial cellulose-poly (acrylic acid) hybrid hydrogels with controllable antimicrobial ability as dressings for chronic wounds. *Polymers* 10, 1323.
- Da Silva, D., Kaduri, M., Poley, M., *et al.*, 2018. Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical implants and theranostic systems. *Chemical Engineering Journal* 340, 9–14.
- Danhier, F., Feron, O., Preat, V., 2010. To exploit the tumor microenvironment: Passive and active tumor targeting of nanocarriers for anti-cancer drug delivery. *Journal of Controlled Release* 148, 135–146.
- Das, R.K., Kasoju, N., Bora, U., 2010. Encapsulation of curcumin in alginate-chitosan-pluronic composite nanoparticles for delivery to cancer cells. *Nanomedicine: Nanotechnology, Biology and Medicine* 6, 153–160.
- Dhalendra, K., Utsav, V., Nagesh, D., *et al.*, 2020. Alginate as promising natural polymer for pharmaceutical, food, and biomedical applications. *Current Drug Delivery* 17, 1–21.
- Ghasemi-Mobarakeh, L., Kolahzadeh, D., Ramakrishna, S., Williams, D., 2019. Key terminology in biomaterials and biocompatibility. *Current Opinion in Biomedical Engineering* 10, 45–50.
- Ghosal, K., Chandra, A., Praveen, G., *et al.*, 2018. Electrospinning over solvent casting: Tuning of mechanical properties of membranes. *Scientific Reports* 8, 1–9.
- Gregor, A., Filová, E., Novák, M., *et al.*, 2017. Designing of PLA scaffolds for bone tissue replacement fabricated by ordinary commercial 3D printer. *Journal of Biological Engineering* 11, 31.
- Gulbake, A., Jain, A., Jain, A., Sahu, A., 2017. Prodrugs and bioconjugate hydrogels: A valuable strategy for the prolonged-delivery of drugs. In *Functional Hydrogels in Drug Delivery*. Taylor and Francis Group.

- Gullotti, E., Yeo, Y., 2009. Extracellularly activated nanocarriers: A new paradigm of tumor targeted drug delivery. *Molecular Pharmaceutics* 6, 1041–1051.
- Gurunathan, T., Mohanty, S., Nayak, S.K., 2015. A review of the recent developments in biocomposites based on natural fibres and their application perspectives. *Composites Part A: Applied Science and Manufacturing* 77, 1–25.
- He, X., Yang, Y., Li, L., *et al.*, 2020. Engineering extracellular matrix to improve drug delivery for cancer therapy. *Drug Discovery Today* 25, 1727–1734.
- Hottot, A., Vessot, S., Andrieu, J., 2004. A direct characterization method of the ice morphology. Relationship between mean crystals size and primary drying times of freeze-drying processes. *Drying Technology* 22, 2009–2021.
- Hu, J., Liu, S., 2010. Responsive polymers for detection and sensing applications: Current status and future developments. *Macromolecules* 43, 8315–8330.
- Huebsch, N., Mooney, D.J., 2009. Inspiration and application in the evolution of biomaterials. *Nature* 462, 426–432.
- Hung, W.-H., Zheng, J.-H., Lee, K.-C., Cho, E.-C., 2019. Doxorubicin conjugated AuNP/biopolymer composites facilitate cell cycle regulation and exhibit superior tumor suppression potential in KRAS mutant colorectal cancer. *Journal of Biotechnology* 306, 149–158.
- Jain, A., Gulbake, A., Shilpi, S., *et al.*, 2013. A new horizon in modifications of chitosan: Syntheses and applications. *Critical Reviews in Therapeutic Drug Carrier Systems* 30, 91–181.
- Jain, A., Hurkat, P., Jain, A., *et al.*, 2018a. Thiolated polymers: Pharmaceutical tool in nasal drug delivery of proteins and peptides. *International Journal of Peptide Research and Therapeutics* 1–12.
- Jain, A., Hurkat, P., Jain, S.K., 2019a. Development of liposomes using formulation by design: Basics to recent advances. *Chemistry and Physics of Lipids* 224, 104764.
- Jain, A., Jain, S.K., 2015. Environmentally responsive chitosan-based nanocarriers (CBNs). In: *Handbook of Polymers for Pharmaceutical Technologies, Biodegradable Polymers*, third ed. John Wiley & Sons, 2015, p. 105.
- Jain, A., Jain, S.K., 2016a. In vitro release kinetics model fitting of liposomes: An insight. *Chemistry and Physics of Lipids* 201, 28–40.
- Jain, A., Jain, S.K., 2016b. Multipronged, strategic delivery of paclitaxel-topotecan using engineered liposomes to ovarian cancer. *Drug Development and Industrial Pharmacy* 42, 136–149.
- Jain, A., Jain, S.K., 2017. Chapter 9: Application potential of engineered liposomes in tumor targeting. In: Grumezescu, A. (Ed.), *Multifunctional Systems for Combined Delivery, Biosensing and Diagnostics*. Elsevier - Health Sciences Division.
- Jain, A., Jain, S.K., 2018. Stimuli-responsive smart liposomes in cancer targeting. *Current Drug Targets* 19, 259–270.
- Jain, A., Jain, S.K., 2013. Engineered chitosan: A potential tool in biomedical applications. *International Journal of Biotechnology and Bioengineering Research*, 4, 1–4.
- Jain, A., Kumari, R., Tiwari, A., *et al.*, 2018b. Nanocarrier based advances in drug delivery to tumor: An overview. *Current Drug Targets* 19, 1498–1518.
- Jain, A., Prajapati, S.K., Kumari, A., Mody, N., Bajpai, M., 2020. Engineered nanosponges as versatile biodegradable carriers: An insight. *Journal of Drug Delivery Science and Technology* 57, 101643.
- Jain, A.J., Sanjay, K., 2016. Liposomes in cancer therapy. In: Carlos, J. (Ed.), *Nanocarrier Systems for Drug Delivery*. New York: Nova Science Publishers.
- Jain, A., Tiwari, A., Verma, A., Jain, S.K., 2018c. Ultrasound-based triggered drug delivery to tumors. *Drug Delivery and Translational Research* 8, 150–164.
- Jain, A., Tiwari, A., Verma, A., Saraf, S., Jain, S., 2019b. Combination cancer therapy using multifunctional liposomes. *Critical Reviews in Therapeutic Drug Carrier Systems* 37, 105–134.
- Jain, D., Bar-Shalom, D., 2014. Alginate drug delivery systems: Application in context of pharmaceutical and biomedical research. *Drug Development and Industrial Pharmacy* 40, 1576–1584.
- Jain, S.K., Jain, A., 2016c. Ligand mediated drug targeted liposomes. In *Liposomal Delivery Systems: Advances and Challenges*. London: Future Medicine Ltd, pp. 144–158.
- Karimi, M., Avci, P., Mobasser, R., Hamblin, M.R., Naderi-Manesh, H., 2013. The novel albumin–chitosan core–shell nanoparticles for gene delivery: Preparation, optimization and cell uptake investigation. *Journal of Nanoparticle Research* 15, 1651.
- Kenar, H., Ozdogan, C.Y., Dumlu, C., *et al.*, 2019. Microfibrous scaffolds from poly (l-lactide-co- ϵ -caprolactone) blended with xeno-free collagen/hyaluronic acid for improvement of vascularization in tissue engineering applications. *Materials Science and Engineering: C* 97, 31–44.
- Kondiah, P.J., Kondiah, P.P., Choonara, Y.E., Marimuthu, T., Pillay, V.A., 2020. 3D bioprinted pseudo-bone drug delivery scaffold for bone tissue engineering. *Pharmaceutics* 12, 166.
- Kumari, A., Jain, A., Hurkat, P., Tiwari, A., Jain, S.K., 2018. Eudragit S100 coated microsponges for colon targeting of prednisolone. *Drug Development and Industrial Pharmacy* 44, 902–913.
- Kumari, A., Jain, A., Hurkat, P., Verma, A., Jain, S.K., 2016. Microsponges: A pioneering tool for biomedical applications. *Critical Reviews in Therapeutic Drug Carrier Systems* 33, 77–105.
- Kumar, B., Murali, A., Bharath, A., Giri, S., 2019. Guar gum modified upconversion nanocomposites for colorectal cancer treatment through enzyme-responsive drug release and NIR-triggered photodynamic therapy. *Nanotechnology* 30, 315102.
- Lim, Y.-M., Gwon, H.-J., Choi, J.-H., *et al.*, 2010. Preparation and biocompatibility study of gelatin/kappa-carrageenan scaffolds. *Macromolecular Research* 18, 29–34.
- Liu, D., Yang, F., Xiong, F., Gu, N., 2016a. The smart drug delivery system and its clinical potential. *Theranostics* 6, 1306.
- Liu, S., Dozois, M.D., Chang, C.N., *et al.*, 2016b. Prolonged ocular retention of mucoadhesive nanoparticle eye drop formulation enables treatment of eye diseases using significantly reduced dosage. *Molecular Pharmaceutics* 13, 2897–2905.
- Liu, G., Li, Y., Yang, L., *et al.*, 2017. Cytotoxicity study of polyethylene glycol derivatives. *RSC Advances* 7, 18252–18259.
- Li, J., Mooney, D.J., 2016. Designing hydrogels for controlled drug delivery. *Nature Reviews Materials* 1, 1–17.
- Maeda, H., Bharate, G., Daruwalla, J., 2009. Polymeric drugs for efficient tumor-targeted drug delivery based on EPR-effect. *European Journal of Pharmaceutics and Biopharmaceutics* 71, 409–419.
- Maeda, H., Sawa, T., Konno, T., 2001. Mechanism of tumor-targeted delivery of macromolecular drugs, including the EPR effect in solid tumor and clinical overview of the prototype polymeric drug SMANCS. *Journal of Controlled Release* 74, 47–61.
- Masulli, M., Renard, D., 2017. *Advances in Physicochemical Properties of Biopolymers (Part 2)*. Bentham Science Publishers.
- Matthews, F.L., Rawlings, R.D., 1999. *Composite Materials: Engineering and Science*. CRC press.
- Meenach, S.A., Hilt, J.Z., Anderson, K.W., 2010. Poly (ethylene glycol)-based magnetic hydrogel nanocomposites for hyperthermia cancer therapy. *Acta Biomaterialia* 6, 1039–1046.
- Mogoşanu, G.D., Grumezescu, A.M., Bejenaru, L.E., Bejenaru, C., 2016. Natural and synthetic polymers for drug delivery and targeting. In *Nanobiomaterials in Drug Delivery*. Elsevier.
- Mohan, S., Oluwafemi, O.S., Kalarikkal, N., Thomas, S., Songca, S.P., 2016. Biopolymers—application in nanoscience and nanotechnology. *Recent Advances in Biopolymers* 1, 47–66.
- Mokhtarzadeh, A., Alibakhshi, A., Yaghoobi, H., *et al.*, 2016. Recent advances on biocompatible and biodegradable nanoparticles as gene carriers. *Expert Opinion on Biological Therapy* 16, 771–785.
- Narayanaswamy, R., Torchilin, V.P., 2019. Hydrogels and their applications in targeted drug delivery. *Molecules* 24, 603.
- Nie, S., 2010. Understanding and overcoming major barriers in cancer nanomedicine. *Nanomedicine* 5, 523–528.
- Panda, P.K., Saraf, S., Tiwari, A., *et al.*, 2019. Novel strategies for targeting prostate cancer. *Current Drug Delivery* 16, 712–727.
- Park, S.-B., Lih, E., Park, K.-S., Joung, Y.K., Han, D.K., 2017. Biopolymer-based functional composites for medical applications. *Progress in Polymer Science* 68, 77–105.
- Parmar, A., Jain, A., Uppal, S., *et al.*, 2018. Anti-proliferate and apoptosis triggering potential of methotrexate-transferrin conjugate encapsulated PLGA nanoparticles with enhanced cellular uptake by high-affinity folate receptors. *Artificial Cells, Nanomedicine, and Biotechnology*. 1–16.

- Patiño-Ruiz, D., Marrugo, L., Reyes, N., Acevedo-Morantes, M., Herrera, A., 2020. Ionotropic gelation synthesis of chitosan-alginate nanodisks for delivery system and in vitro assessment of prostate cancer cytotoxicity. *International Journal of Polymer Science*. 2020.
- Patra, J.K., Das, G., Fraceto, L.F., *et al.*, 2018. Nano based drug delivery systems: Recent developments and future prospects. *Journal of nanobiotechnology* 16, 71.
- Prajapati, S.K., Jain, A., Jain, A., Jain, S., 2019a. Biodegradable polymers and constructs: A novel approach in drug delivery. *European Polymer Journal* 120, 109797.
- Prajapati, S.K., Jain, A., Shrivastava, C., Jain, A.K., 2019b. Hyaluronic acid conjugated multi-walled carbon nanotubes for colon cancer targeting. *International Journal of Biological Macromolecules* 123, 691–703.
- Prajapati, S.K., Malaiya, A., Kesharwani, P., Soni, D., Jain, A., 2020a. Biomedical applications and toxicities of carbon nanotubes. *Drug Chem Toxicol.* 1–16.
- Prajapati, S.K., Mody, N., Jain, A., 2020b. Hyaluronic Acid: Biodegradable Material of Choice for Drug Delivery Applications. *Hyaluronic Acid: History, Uses and Health Effects*. Nova Science Publisher, 77–105. ISBN 978-1-53617-059-7.
- Pulakkat, S., Balaji, S.A., Rangarajan, A., Raichur, A.M., 2016. Surface engineered protein nanoparticles with hyaluronic acid based multilayers for targeted delivery of anticancer agents. *ACS applied materials & interfaces* 8, 23437–23449.
- Qin, J., Wei, X., Chen, H., *et al.*, 2018. mPEG-g-CS-modified PLGA nanoparticle carrier for the codelivery of paclitaxel and epirubicin for breast cancer synergistic therapy. *ACS Biomaterials Science & Engineering* 4, 1651–1660.
- Rahaiee, S., Hashemi, M., Shojaosadati, S.A., Moini, S., Razavi, S.H., 2017. Nanoparticles based on crocin loaded chitosan-alginate biopolymers: Antioxidant activities, bioavailability and anticancer properties. *International Journal of Biological Macromolecules* 99, 401–408.
- Rajan, M., Raj, V., Al-Arfaj, A.A., Murugan, A., 2013. Hyaluronidase enzyme core-5-fluorouracil-loaded chitosan-PEG-gelatin polymer nanocomposites as targeted and controlled drug delivery vehicles. *International Journal of Pharmaceutics* 453, 514–522.
- Rehm, B.H., 2010. Bacterial polymers: Biosynthesis, modifications and applications. *Nature Reviews Microbiology* 8, 578–592.
- Rode, M.P., Batti Angulski, A.B., Gomes F.A., *et al.*, 2018. Carrageenan hydrogel as a scaffold for skin-derived multipotent stromal cells delivery. *Journal of biomaterials applications*, 33, 422–434.
- Rodrigues, S., Dionisio, M., López, C.R., Grenha, A., 2012. Biocompatibility of chitosan carriers with application in drug delivery. *Journal of Functional Biomaterials* 3, 615–641.
- Saraf, S., Jain, A., Hurkat, P., Jain, S.K., 2016. Topotecan liposomes: A visit from a molecular to a therapeutic platform. *Critical Reviews in Therapeutic Drug Carrier Systems* 33, 401–432.
- Saraf, S., Jain, A., Tiwari, A., Verma, A., Jain, S.K., 2020a. Engineered liposomes bearing camptothecin analogue for tumor targeting: In vitro and ex-vivo studies. *Journal of Liposome Research*. 1–32.
- Saraf, S., Jain, A., Tiwari, A., *et al.*, 2020b. Advances in liposomal drug delivery to cancer: An overview. *Journal of Drug Delivery Science and Technology*. 101549.
- Senapati, S., Mahanta, A.K., Kumar, S., Maiti, P., 2018. Controlled drug delivery vehicles for cancer treatment and their performance. *Signal Transduction and Targeted Therapy* 3, 1–19.
- Shao, L., Tekedereli, I., Wang, J., *et al.*, 2012. Highly specific targeting of the TMPRSS2/ERG fusion gene using liposomal nanovectors. *Clinical Cancer Research* 18, 6648–6657.
- Shukla, T., Upmanyu, N., Pandey, S.P., Sudheesh, M., 2019. Site-specific drug delivery, targeting, and gene therapy. In *Nanoarchitectonics in Biomedicine*. Elsevier.
- Soltan, N., Ning, L., Mohabatpour, F., Papagerakis, P., Chen, X., 2019. Printability and cell viability in bioprinting alginate dialdehyde-gelatin scaffolds. *ACS Biomaterials Science & Engineering* 5, 2976–2987.
- Song, W., Su, X., Gregory, D.A., *et al.*, 2018. Magnetic alginate/chitosan nanoparticles for targeted delivery of curcumin into human breast cancer cells. *Nanomaterials* 8, 907.
- Spasojevic, M., Bhujbal, S., Paredes, G., *et al.*, 2014. Considerations in binding diblock copolymers on hydrophilic alginate beads for providing an immunoprotective membrane. *Journal of Biomedical Materials Research Part A* 102, 1887–1896.
- Subudhi, M.B., Jain, A., Jain, A., *et al.*, 2015. Eudragit S100 coated citrus pectin nanoparticles for colon targeting of 5-fluorouracil. In: *Materials*, 8, pp. 832–849.
- Sun, X., Liu, C., Omer, A., *et al.*, 2019a. pH-sensitive ZnO/carboxymethyl cellulose/chitosan bio-nanocomposite beads for colon-specific release of 5-fluorouracil. *International Journal of Biological Macromolecules* 128, 468–479.
- Sun, X., Liu, C., Omer, A., Yang, L.-Y., Ouyang, X.-K., 2019b. Dual-layered pH-sensitive alginate/chitosan/kappa-carrageenan microbeads for colon-targeted release of 5-fluorouracil. *International Journal of Biological Macromolecules* 132, 487–494.
- Tiwari, A., Jain, A., Verma, A., Panda, P., Jain, S.K., 2019. Alginate-based composites in drug delivery application. In *ALGINATES Versatile Polymers in Biomedical Applications and Therapeutics*. Apple Academic Press.
- Tiwari, G., Tiwari, R., Sriwastawa, B., *et al.*, 2012. Drug delivery systems: An updated review. *International Journal of Pharmaceutical Investigation* 2, 2–11.
- Torres, F.G., Troncoso, O.P., 2020. Starch based Polymers for Drug Delivery Applications. *Polysaccharides in Advanced Drug Delivery*. CRC Press.
- Verma, A., Jain, A., Tiwari, A., Jain, S.K., 2018. Emulgels: Application Potential in Drug Delivery. In *Functional Biopolymers*. Springer.
- Verma, A., Sharma, G., Jain, A., *et al.*, 2019. Systematic optimization of cationic surface engineered mucoadhesive vesicles employing Design of Experiment (DoE): A preclinical investigation. *International Journal of Biological Macromolecules* 133, 1142–1155.
- Wang, M., 2003. Developing bioactive composite materials for tissue replacement. *Biomaterials* 24, 2133–2151.
- Wang, W., Meng, Q., Li, Q., *et al.*, 2020. Chitosan derivatives and their application in biomedicine. *International Journal of Molecular Sciences* 21, 487.
- Wei, M., Gao, Y., Li, X., Serpe, M.J., 2017. Stimuli-responsive polymers and their applications. *Polymer Chemistry* 8, 127–143.
- Yang, G., Xiao, Z., Long, H., *et al.*, 2018. Assessment of the characteristics and biocompatibility of gelatin sponge scaffolds prepared by various crosslinking methods. *Scientific Reports* 8, 1–13.
- Zarrintaj, P., Manouchehri, S., Ahmadi, Z., *et al.*, 2018. Agarose-based biomaterials for tissue engineering. *Carbohydrate polymers* 187, 66–84.
- Zhang, B., Zhang, P.B., Wang, Z.L., Lyu, Z.W., Wu, H., 2017. Tissue-engineered composite scaffold of poly (lactide-co-glycolide) and hydroxyapatite nanoparticles seeded with autologous mesenchymal stem cells for bone regeneration. *Journal of Zhejiang University-SCIENCE B* 18, 963–976.
- Zhang, B., Wan, S., Peng, X., *et al.*, 2020a. Human serum albumin-based doxorubicin prodrug nanoparticles with tumor pH-responsive aggregation-enhanced retention and reduced cardiotoxicity. *Journal of Materials Chemistry B* 8, 3939–3948.
- Zhang, W., Xu, W., Lan, Y., *et al.*, 2019. Antitumor effect of hyaluronic-acid-modified chitosan nanoparticles loaded with siRNA for targeted therapy for non-small cell lung cancer. *International Journal of Nanomedicine* 14, 5287.
- Zhang, Z., Zhou, S., Zhang, Y., Wu, D., Yang, X., 2020b. The dual delivery of growth factors and antimicrobial peptide by PLGA/GO composite biofilms to promote skin-wound healing. *New Journal of Chemistry* 44, 1463–1476.

Covalent and Electrostatic Protein-Polysaccharide Systems for Encapsulation of Nutraceuticals

Hadis Rostamabadi, Seid Reza Falsafi, and Seid Mahdi Jafari, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran

© 2021 Elsevier Inc. All rights reserved.

Introduction

The prospects of nanotechnology and its prompt integration with the food/pharmaceutical field have led to the development of effectual nutraceutical/drug delivery systems with targeted release properties (Assadpour *et al.*, 2020). However, notwithstanding the accumulated attempts on the bioactive delivery systems, the poor applicability of encapsulation approaches have caused multiple hindrances, which set limits to their clinical applications (Peltonen, 2018; Rostamabadi *et al.*, 2019a,b). In this scenario, numerous promising nutraceutical candidates are admitting the fate of being adversely developed, owing to the insufficiency of some carrier matrices (Falsafi *et al.*, 2020b).

The prerequisites for the potential encapsulation of bioactives/drugs are the maximization of absorptive cellular uptake and physical/chemical stabilization of the therapeutics at all steps before reaching their destination (Abaee *et al.*, 2017; Jafari and McClements, 2017; Rostamabadi *et al.*, 2020a, 2019a). To design and develop carrier matrices equipped with these attributes, the focus of encapsulation strategy is on superior vehicles and materials for nutraceuticals delivery (Esfanjani and Jafari, 2016).

Nowadays, numerous novel and efficient biopolymer-based delivery matrices have been engineered through encapsulation technology to meet the ever-increasing demands of various fields. In this line, nature-inspired polysaccharides and proteins from plants, animals, and even microbial origins (such as bacteria, yeast, or microalgae) are extensively utilized as functional biopolymer matrices in the food and pharmaceutical realm (Aditya *et al.*, 2017; Assadpour and Jafari, 2019; Jacob *et al.*, 2018; Joye and McClements, 2014). Instances comprise plant- or microbial-derived polysaccharides e.g., gum arabic, pectins, chitosan, alginate, and xanthan gum. On the protein side, plant-derived proteins like soybean, pea, or canola and animal-based ones e.g., gelatins and whey proteins have found common application (Bolhassani *et al.*, 2014; Gupta and Nayak, 2015; Park *et al.*, 2017).

Recently, covalent and non-covalent protein-polysaccharide systems have gained a great deal of attention for the delivery and protect of a vast verity of bioactive ingredients (e.g., phenolics, carotenoids, volatile oils, flavors, etc.). Notwithstanding the fact that the polysaccharide and protein matrices individually possess a range of beneficial features, e.g., the potential to serve as thickening, stabilizing, or water-holding agents (Damodaran, 2005; Doublier *et al.*, 2000; Samant *et al.*, 1993), they can be made to assemble into hierarchically higher-ordered arrangements, which can provide novel (bio)functionalities. These properties render both covalent and non-covalent protein-polysaccharide systems as effective pair biopolymers for the development of novel nutraceutical formulations. In this line, Table 1 summarizes the application fields of covalent and non-covalent protein-polysaccharide systems. The covalent linkage is attained by a Maillard-type reaction lead to the formation of protein-polysaccharide conjugates with strong heat stability (Fechner *et al.*, 2007; Shah *et al.*, 2012b; Yi *et al.*, 2014). In a conjugate system of protein-polysaccharide, the polysaccharide fraction typically endows potent steric and sometimes electrostatic repulsion, and the protein molecule of the conjugate could be attached to hydrophobic surfaces. Nevertheless, the reaction circumstances, e. g., pH or temperature, should be precisely controlled to attain a desirable reaction (George *et al.*, 2020; Li and Gu, 2014; Shah *et al.*, 2012a; Xu *et al.*, 2013). In the case of non-covalent systems of proteins and polysaccharides, the driving forces include electrostatic, hydrophobic, H₂ linkage, as well as Van der Waals interactions, which induce the generation of coacervates (Eratte *et al.*, 2015; Pham *et al.*, 2020, 2021).

This article highlights the applicability of polysaccharide-protein systems fabricated through both covalent and electrostatic interactions in designing nutraceutical delivery systems to exploit their benefits in nano/micro-encapsulation, shield, and delivery of different nutraceuticals.

Proteins

Food-grade proteins have revolutionized bioactive delivery by offering a myriad of unique physical/chemical and structural features to delivery vehicles (Gaber *et al.*, 2018; Weiss *et al.*, 2019). Due to the presence of multiple functional units in the primary sequences of polypeptides, protein-based matrices could be utilized to create diverse interactions with bioactive agents, providing a range of possibilities for nutraceutical delivery (Elzoghby *et al.*, 2011, 2012). Protein-based carriers are acceptable as metabolizable nature-inspired components, as hydrolysis of protein molecules by gastrointestinal enzymes lead to the generation of bioactive peptides, which might exert various physiological influences in vivo (Chen *et al.*, 2006). A number of strategies have been employed to design protein-based delivery systems with outstanding release manners, bioactivities, targeting capacity, as well as safety (Eratte *et al.*, 2015; Sriprabhom *et al.*, 2019; Yang *et al.*, 2015a).

Proteins can inherently hinder the flocculation of emulsion particles as a result of their high attitude to adsorb onto the hydrophilic-hydrophobic interfaces and creating a comparatively thin adsorbed cover by subsequent unfolding (approximately 2–6 nm) and

Table 1 Some examples concerning the application fields of protein-polysaccharide pair systems

Field	Usage	Reference
Medicine/ pharmacy	● Drug/gene delivery. ● Extraction or purification of different compounds	(Gaber <i>et al.</i> , 2018; Nitta and Numata, 2013)
Food science	● Encapsulating agents for nutraceutical delivery with improved stability, viability, sustained/controlled release, as well as taste masking. ● Textural modifiers and stabilizing agents for dispersed media.	(Aylanc <i>et al.</i> , 2020; Devi and Maji, 2011; Ghasemi <i>et al.</i> , 2018; Koupantsis <i>et al.</i> , 2014)
Materials science	● Composites for biofunctional and biodegradable packaging.	(Weiss <i>et al.</i> , 2019)
Agriculture	● Encapsulating agents for controlled release of various nutrients, agrochemicals, or pheromones.	(Campos <i>et al.</i> , 2015; Kong <i>et al.</i> , 2009)

generating electrostatic and steric stabilization (Dickinson, 2010; Jacob *et al.*, 2018; Yang *et al.*, 2015b). The van der Waals attractive forces among particles in a colloidal system dominate the electrostatic repulsion, simultaneously the electric charge of protein molecules is the main is the most important reason that jeopardize the stability of colloidal system. At the isoelectric point (pI) the positive and negative charges are balanced, diminishing repulsive electrostatic forces and leading to the aggregation and/ or precipitation (Vadavik and Christian, 2008). Furthermore, numerous studies on proteins revealed how environmental conditions e. g., heat treatment, pH value, ionic strength, as well as polymer concentration affect the pI (Liu *et al.*, 2016; Sripabloom *et al.*, 2019).

Polysaccharides

Naturally occurring polysaccharides are obtained from different resources from animal origins (e.g., chitosan), algal origins (such as alginate), plant origins (like pectin or guar gum), as well as microbial sources (e.g., xanthan gum or dextran) and have intrinsic bioactivity due to their anti-bacterial, anti-inflammatory, as well as mucoadhesive properties (Liu *et al.*, 2008; Reis *et al.*, 2006). Polysaccharides possess numerous reactive units, different molecular weights, plenty of chemical compositions, contributing to their diversity in configuration and in attribute (Rostamabadi *et al.*, 2019c,d). Polysaccharides could be grouped into two main classes including polyelectrolytes and non-polyelectrolytes; the former could be further classified into negatively charged polysaccharides (such as pectin, alginate, hyaluronic acid, etc.) and positively charged ones (e.g., chitosan) (Du *et al.*, 2004; Liu *et al.*, 2007). As nature-inspired components, polysaccharides are hydrophilic, biodegradable, greatly stable, low-cost, safe, and non-toxic. Polysaccharides mostly possess hydrophilic domains e. g., hydroxyl, carboxyl, as well as amino units that can create non-covalent linkages with biological tissues such as epithelia or mucous membranes, rendering bioadhesion (Falsafi *et al.*, 2018, 2019; Rostamabadi *et al.*, 2019c). It is noteworthy that the bioadhesive polysaccharides such as alginate, chitosan, starch, etc. could extend the residence time and improve the absorbance of entrapped bioactives in vivo (Lee *et al.*, 2000; Rubinstein, 2000; Sinha and Kumria, 2001).

Protein-Polysaccharide Systems

Engineering protein-polysaccharide systems for nutraceutical delivery has attained momentum by virtue of their biochemical/ biophysical attributes over synthetic delivery cargos, i.e., biocompatibility, scalability, tunability, as well as lack of toxicity (Doublier *et al.*, 2000; Schmitt and Turgeon, 2011). These structures, have been widely implemented to develop an efficient host for a range of nutraceutical molecules such as curcuminoids, carotenoids, vitamins, polyphenols, essential oils, etc. (Gaber *et al.*, 2018; Gentile, 2020). In this line, following sections will be discussed the application of covalent and electrostatic protein-polysaccharide systems for nutraceutical delivery.

Conjugated Systems

Covalent interactions between proteins and polysaccharides are greatly specific and strong, creating a permanent, irreversible protein-polysaccharide linkage (Shah *et al.*, 2012b; Yi *et al.*, 2014). This interaction is recognized as protein-polysaccharide glycosylation, which chemically created by amino residues of the protein molecule and carboxylic units of the polysaccharide moiety, establishing a covalently bound amide (George *et al.*, 2020; Li and Gu, 2014). The main reason for such reaction is principally relevant to the presence of lysine residues, which induces a Maillard-type reaction with the reducing sugars of the polysaccharide molecule, upon properly low water-activity and heat treatment at an incubation period of around a few hours (Akhtar and Ding, 2017; De Fenoyl *et al.*, 2018; Zhang *et al.*, 2020).

Contrary to the non-covalent interactions, the protein-polysaccharide conjugates or covalent systems are not responsive to ionic strength and pH variations. Interestingly, the formation of glycosylated protein-polysaccharide conjugates can be considerably

influenced by the length of the polysaccharide chain and the nature of the protein molecule. In the view point of protein structure, the unfolded proteins like casein typically react more promptly with polysaccharide structure than folded ones e.g., lysozyme (Dai *et al.*, 2018; George *et al.*, 2020; Lopes *et al.*, 2019; Wijaya *et al.*, 2017).

One substantial restriction of the conjugation process could be the loss of protein functionality, as most of the lysyl unites are covered by the polysaccharide moiety, especially concerning conjugates of proteins with mono or oligosaccharides. Nonetheless, the Maillard conjugates of proteins and polysaccharides typically demonstrate an excellent emulsifying capacity, anti-microbial property, and even heat stability (Gentile, 2020).

Electrostatic Complexes

The complexation mechanism between macromolecules mainly stems from the electrostatic interactions between diverse oppositely charged biopolymers, especially a protein and a polysaccharide. The soluble complexes of protein-polysaccharide pairs then continue the aggregation and reduction the free energy of the system until their size/surface characteristics offer a way to insolubilization, consequently causing liquid-liquid phase separation and coacervation through non-covalent and H-bonding interactions (Dai *et al.*, 2018; Schmitt and Turgeon, 2011; Weinbreck *et al.*, 2004a). Protein chain carries a negative or positive surface charge relying on the pH range of the protein-polysaccharide system. The positive/negative zeta potential of the protein molecule oriented from the presence of various amino acid groups within the protein structure and their mode of ionization at diverse pHs (de Oliveira *et al.*, 2020; Yeo *et al.*, 2005a). Food proteins with a pI approximately 5 could create complex coacervates with anionic polysaccharides e.g., pectin (with pKa 3.5) in the intermediate pH range, where both macromolecules possess opposite net charges: pH below the pI of the protein but above the pKa of the polysaccharide (Eratte *et al.*, 2015; Koupantsis *et al.*, 2014).

The electrostatic complexes between proteins and polysaccharides are mainly affected by a range of parameters, including pH and ionic strength of the medium, biopolymer concentration or molecular weight, and protein-to-polysaccharide ratio (Aylanc *et al.*, 2020; Esfahani *et al.*, 2019). A number of other factors like temperature, pressure, flexibility, charge density, and even stirring have also been demonstrated to affect the coacervation phenomenon (Chen *et al.*, 2018; Xie *et al.*, 2019).

It is worthwhile to note that there are several instances in the literature where the two polymeric poly-ions are proteins (Clarke *et al.*, 2006; Croguennec *et al.*, 2017; Nigen *et al.*, 2007). Intriguingly, same-charged complex coacervates have been also stated even between two positively charged polyelectrolytes as a result of suppressing long-range electrostatic repulsion (Kim *et al.*, 2016). Generally, coacervates are defined as reversible structures, which form or segregate as the polymeric solution and/or environmental circumstances are changed (Cooper *et al.*, 2005; Kayitmazer *et al.*, 2013; Schmitt and Turgeon, 2011).

Characterization Approaches of Protein-Polysaccharide Systems

In the case of glycosylated protein-polysaccharide conjugates, electrophoresis is one of the most widely utilized approaches for characterization of protein-polysaccharide systems. The synthesis of conjugate structures through the covalent bonds between the amine units of the protein molecule and the carbonyl/carboxyl units of the polysaccharide moiety might be corroborated by using sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) technique (Fechner *et al.*, 2007; Shah *et al.*, 2012a; Yi *et al.*, 2014).

A number of methods have been employed to investigate the degree of protein modification and the extent of the Maillard reaction. The latter is determined by the average number of lysine residues, which react with polysaccharide molecule. In this context, the o-phthalaldehyde (OPA) is a colorimetric assay for indirect determination of the extent of the Maillard process relying on the reaction between the OPA and the free amine units of the protein molecule (Kim and Shin, 2020; Tu *et al.*, 2020). The 2,4,6-Trinitrobenzenesulfonic acid (TNBS) test is another prompt and sensitive chemical method applied to quantify the free primary amino units. The reaction between TNBS and amine groups lead to the generation of a highly chromogenic product, which could be measured at 335 nm (Dong *et al.*, 2020; Shi *et al.*, 2019). The extent of the Maillard reaction can also be quantified using furosine assay (ϵ -N-furoylmethyl-L-lysine), followed by acid hydrolysis of the Maillard reaction products (Li *et al.*, 2020; Michalska *et al.*, 2016).

Other approaches commonly utilized in conjugate characterization are circular dichroism (CD), dynamic light scattering (DLS), Matrix Assisted Laser Desorption Ionization-Time of Flight-Mass Spectrometry (MALDI-TOF MS), fluorescence spectroscopy, imaging approaches (e. g., atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM)), fourier transform infrared spectroscopy (FTIR), and colorimetric assays (Rostamabadi *et al.*, 2020b; de Oliveira *et al.*, 2016).

Electrostatic protein-polysaccharide as potential bioactive carriers are also characterized through several experimental approaches, as summarized in Table 2.

Application of Protein-Polysaccharide Systems for Encapsulation of Different Bioactive Compounds

Biopolymeric delivery systems based on covalent conjugates and complex coacervates have been widely utilized to develop micro/nanocapsules of unique (bio)functional attributes e.g., providing a homogeneous distribution of mainly non-polar ingredients in polar media, enabling controlled bioactive release, as well as hindering degradation of sensitive bioactive molecules (Assadpour

Table 2 Characterization methods of an electrostatic protein–polysaccharide system

Technique	Explanations	References
Capillary electrophoresis (CE)	Determining the binding parameters of protein-polysaccharide complexes according to their size and charge.	Girard <i>et al.</i> (2003)
DLS	- Providing the average size of the coacervate particles - Representing the average hydrodynamic radius (Rh) of the protein-polysaccharide system that is attained from the peak position of their Rh distribution curves. - Measuring the electrophoretic mobility of the system via a laser Doppler electrophoresis.	Weinbreck <i>et al.</i> (2004b) Mekhloufi <i>et al.</i> (2005)
Confocal Laser Scanning Microscopy (CLSM)	- Offering information about the structure and nature of the protein-polysaccharide system. - Clarifying the main discrepancies between dispersions of two oppositely charged biopolymers. - Investigating fluorescence recovery after photo-bleaching (FRAP).	Garcia-Herraz <i>et al.</i> (2012); Tromp <i>et al.</i> (2001); Weinbreck <i>et al.</i> (2004b)
Diffusing Wave Spectroscopy (DWS)	Assessing the rheological features and stability of the complex medium.	Schmitt <i>et al.</i> (2001)
Zeta potential	Calculating the absolute value of the produced complex.	Weinbreck <i>et al.</i> (2004b)
Turbidimetry using a UV–Visible spectrophotometer or a simple turbidity-meter	- Offering a chance to adjust the transparency/turbidity of the system. - Effective way to evaluate the coacervate formation. - Possibility to determine the optimum polymer ratio and pH value for the complexation. - The maximum turbidity of the system is typically relevant to the maximum interactions between biopolymers, while at the maximum interaction (after centrifugation), the turbidity of the supernatant diminished to minimum as a result of the precipitation/sedimentation of the coacervate.	Devi and Kakati (2013)
Small Angle Static Light Scattering (SALS)	Efficient technique for obtaining both structural and rheological information (e. g., size diameter, morphology, orientation, as well as spatial distribution).	Laneville <i>et al.</i> (2006)
¹ H Nuclear Magnetic Resonance spectroscopy (NMR)	The structural study of complexes in aqueous system relying on mobility determination of H₂O molecules through relaxation time analysis (electrostatic interactions of the system is highly effective on the motion of the H₂O molecules).	Ducel <i>et al.</i> (2008)
Small Angle Neutron Scattering technique (SANS)	Characterizing the size, shape, water content, and internal organization of coacervates depending on their charge density.	Schmidt <i>et al.</i> (2009)
Small-angle X-ray scattering (SAXS)	Possibility of investigating the structural changes of complex coacervates as a function of pH, ionic strength, or polysaccharide: protein ratio.	Weinbreck <i>et al.</i> (2004c)
Phase contrast microscopy	Possibility of controlling the structural variations in developed coacervates dispersions.	Girard <i>et al.</i> (2003)
Viscometry	Evaluating the relative viscosity of the protein-polysaccharide system using a viscometer/rheometer to determine the optimum polymer ratio and pH value for the complexation.	Devi and Kakati, (2013)
Raman microspectroscopy	Controlling the complex formation between protein and polysaccharide.	Chourpa <i>et al.</i> (2006)
CD approach	Study of the protein conformational alterations following the complexation via a Far-UV circular dichroism.	Mekhloufi <i>et al.</i> (2005)
Kinetics of Phase Separation	Characterizing the influence of different parameters e. g., pH, ionic strength, or polysaccharide: protein ratio on the complexation.	Weinbreck <i>et al.</i> (2004c)
FTIR spectroscopy	- Evaluating the extent of interactions among protein, polysaccharide, and other formulation ingredients within vehicle matrix. - Determining the successfulness of the encapsulation process using coacervate.	Falsafi <i>et al.</i> (2019); Hifumi <i>et al.</i> (2016)
X-Ray diffraction (XRD) analysis Imaging approaches	- Crystallographic study of the complexes. - Application of AFM, SEM, and TEM to study morphological properties, size, and homogeneity of the protein-polysaccharide particles.	Falsafi <i>et al.</i> (2018) Falsafi <i>et al.</i> (2020a)

et al., 2017; Assadpour and Jafari, 2018). One of the main goals of the encapsulation strategies is to shield nutraceuticals from environmental stresses e.g., oxidation, extreme pHs/temperatures, digestive enzymes, etc. (Rostamabadi *et al.*, 2019c, 2020c). This is particularly crucial when developing (bio)functional food products or other bioactive formulations to ensure that the

nutraceutical ingredients preserve their bioactivity/(bio)functionality through processing conditions, storage time, and more importantly in vivo (Boostani and Jafari, 2020; Dima *et al.*, 2020). Such biologically active agents include liposoluble carotenoids (Rostamabadi *et al.*, 2019e), hydrophobic/hydrophilic vitamins (Hsu *et al.*, 2019), essential oils (Esfahani *et al.*, 2019), flavors (Xiao *et al.*, 2019), curcuminoids (Park *et al.*, 2018), oils high in essential ω -3 fatty acids (Chen *et al.*, 2018), etc. Protein-polysaccharide conjugates and coacervates has also been employed to entrap other bioactives i.e., probiotics (Eratte *et al.*, 2015), anti-bacterials (Amara *et al.*, 2017), as well as agricultural components (Dai *et al.*, 2017; Weiss *et al.*, 2019).

Phenolic Compounds

In a recent study by Xie *et al.* (2019), curcumin was incorporated into ovalbumin- κ -carrageenan nanocomplexes (at pH 2.6–3.4) with a slow release upon gastric phase and a potent capability for delivery in the simulated intestinal tract. More recently, Fan *et al.* (2018) produced spherical Maillard conjugate nanoparticles based on bovine serum albumin (BSA) and dextran for curcumin delivery and indicated that the curcumin-encapsulated nanoparticles had higher oxidative and pH stability (at pH 2.0–7.0) as compared to free bioactive. It is worth mentioning that the excellent physicochemical stability of the protein-polysaccharide nanoparticles was probably related to the steric stabilizing impact of the water-soluble dextran conjugated to the protein matrix, designing a dextran-shell BSA-core configuration. The dextran shell properly repelled the proteolysis mechanism in both gastric and intestinal phases, and could improve the physical/chemical stability of the embedded curcumin upon digestion. Wang *et al.* (2016), investigated the behavior of mixtures of BSA and dextran under dry heating of the protein-polysaccharide powder (for 48 h at $\sim 60^\circ\text{C}$ and relative humidity of 79%) for the encapsulation and protection of curcumin-loaded O/W emulsions. The authors noted that the emulsion stability hinges upon both the bioactive concentration and oil volume fraction. Curcumin-loaded emulsions was found to be highly stable at both neutral and acidic conditions probably due to the proper integration into the vehicle and suitable cohesiveness of the interfacial film, preventing the bioactive degradation, precipitation, as well as diffusion to aqueous part. Moreover, the presence of conjugate systems in curcumin-enriched carriers could potentially enhance (4.8 times) the oral bioavailability of the bioactive in mice and promote its absorption in vivo. Dai *et al.* (2018) also designed ternary complexes of zein, propylene glycol alginate, and surfactant (lecithin or rhamnolipid) using anti-solvent co-precipitation method (at pH 4.0) and studied the potential application of these systems for delivery of curcumin and increasing its (bio)stability and bioaccessibility. It was illustrated that the presence of surfactant in complex particles could increase both photo-stability and bioaccessibility of the bioactive. The bioactive bioaccessibility enhanced from 25% when only protein was utilized as vehicle matrix to approximately 80% in the complex particles.

In a study from Zhou *et al.* (2012), a novel type of complex coacervation core micelles based on gelatin-dextran conjugates was utilized for effectual delivery of tea polyphenol. The protein-polysaccharide blend was dry-heated at 60°C upon relative humidity of 79% (24 h) to prepare Maillard-type conjugates. Subsequently, the bioactive solution was added to the produced conjugates at a desired pH value to generate complex coacervation core micelles (at room temperature). Contrary to the pure protein or non-heated protein-polysaccharide blends that displayed an obvious precipitation in the presence of the bioactive polyphenol (Fig. 1(A–C)), the polyphenol-loaded protein-polysaccharide conjugates at pH 5.0 developed a homogenous dispersion of narrow particle size distribution (Fig. 1(A, B)). It was postulated that the polysaccharide fraction in the conjugate system by virtue of its stabilizing capacity through the steric hindrance effects caused a lower aggregation of the protein-polyphenol insoluble core. Li and Gu (2014) fabricated self-assembled ovalbumin-dextran conjugate nanoparticles to encapsulate and promote the bioavailability of bioactive (–)-epigallocatechin gallate (EGCG). The conjugate was blended with the bioactive solution at pH 5.2 following heating at 80°C for about 1 h and the self-assembled nanoparticles was further cross-linked by glutaraldehyde at ambient condition for ~ 24 h. The bioactive-entrapped protein-polysaccharide nanostructures were spherical in morphology with loading efficiencies and particle sizes of $\sim 23\%$ – 30% and 285–339 nm, respectively. Interestingly, the apparent permeability coefficient of the bioactive on Caco-2 monolayers was considerably enhanced following encapsulation.

Carotenoids

As one of the most important carotenoids, β -carotene was entrapped into conjugate nanoparticles based on β -lactoglobulin and dextran using a homogenization-evaporation technique to increase its solubility, heat stability, and even bioavailability (Yi *et al.*, 2014). The carotenoid-loaded nanoparticles had potent pH-stability against aggregation upon in-vitro and showed notable release rate and permeability coefficient on Caco-2 cells. β -carotene has been also suitably embedded into whey protein-beet pectin conjugates, where the pH range, metal chelator, free radical scavenger, as well as interfacial properties influenced the carotenoid oxidative stability (Xu *et al.*, 2013). Xu *et al.* (2014) used a whey protein-beet pectin conjugate system for β -carotene encapsulation and clarified that the biostability of conjugate-stabilized emulsions i.e., resistivity to droplet coalescence or flocculation dramatically promoted during in vitro digestion. In another attempt, an O/W emulsion stabilized by casein-dextran conjugates was utilized to encapsulate bioactive lutein. The authors revealed the high stability of designed emulsions to isoelectric flocculation at pHs from 3.0 to 7.0, owing to the capability of the dextran matrix to generate strong steric repulsions overcoming any attractive interactions in the system. However, the application of Maillard conjugates did not influence the carotenoid bioaccessibility (Gumus *et al.*, 2016). Jain *et al.* (2016) demonstrated that β -carotene-embedded casein-gum tragacanth coacervates cross-linked with genipin successfully fabricated at pH 4.35 and protein: polysaccharide ratio of 2:1 (Jain *et al.*, 2016). The prepared

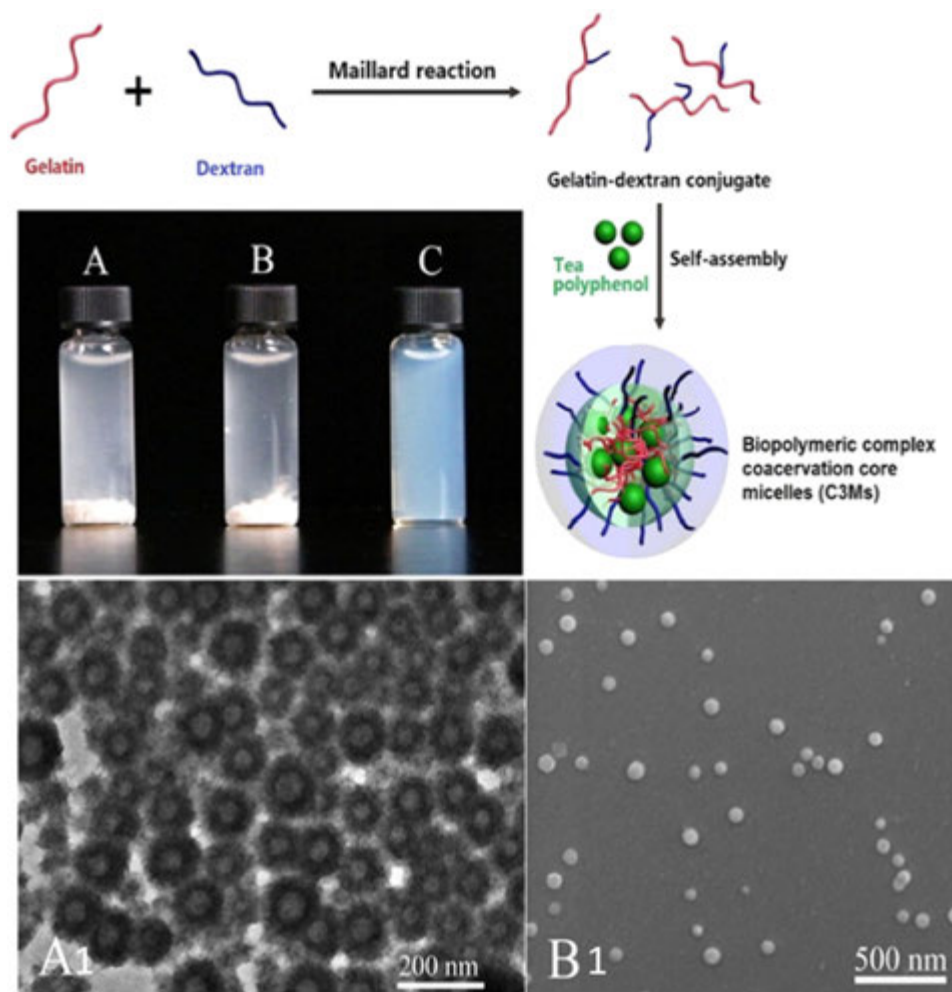


Fig. 1 Images of the gelatin-polyphenol blend (A); gelatin-dextran-polyphenol blend (B); and the complex coacervation core micelles comprised of the gelatin-dextran conjugates and polyphenol (C) (at protein to polysaccharide weight ratio of 1:1 and pH 5.0); TEM (A₁) and SEM (B₁) micrographs of the complex coacervation core micelles comprised of the gelatin-dextran conjugates and polyphenol. Reproduced from Zhou, H., Sun, X., Zhang, L., *et al.*, 2012. Fabrication of biopolymeric complex coacervation core micelles for efficient tea polyphenol delivery via a green process. *Langmuir* 28 (41), 14553–14561. Available at: <https://doi.org/10.1021/la303062j>.

microcapsules possessed particle size of $\sim 160 \mu\text{m}$, encapsulation efficiency of $\sim 79\%$, as well as coacervates yield of $\sim 83\%$. As compared to β -carotene dispersed in oil, the engineered coacervates could powerfully inhibit the degradation and lipid oxidation of the carotenoid during the storage time (2 months). In another study, a lipid extract rich in astaxanthin (obtained from shrimp waste) was encapsulated in gelatin-cashew gum complexes with high water solubility of ~ 28.6 and relatively low entrapment efficiency of around 60% (at pH 4.0–4.5) (Gomez-Estaca *et al.*, 2016). The coacervation process preserved about 47% of the bioactive following 43 days; whilst, the free carotenoid was almost completely decomposed (approximately 9% left). The astaxanthin-loaded freeze-dried microcapsules also incorporated in plain yogurt sample (as a model food matrix) with great coloring capacity, as the corresponding orange color was homogeneously dispersed through the food system and no indication of phase separation was detected.

Bioactive Vitamins

Other biologically active ingredients have also been embedded in protein-polysaccharide conjugates and coacervates. For example, the possibility of stabilizing double emulsions (water-in-oil-in-water type, W/O/W) using sodium caseinate-dextran conjugates to enhance the stability and release properties of vitamin B₁₂ was investigated by Fechner *et al.* (2007). As compared to the sodium caseinate-stabilized emulsions, the double emulsions stabilized by Maillard conjugates indicated smaller size distribution and better pH-stability (at pH 4.0) mainly due to the presence of an additional biopolymer layer around oil droplets and thus leading to better steric stabilization and hindering emulsion particles from aggregation/coalescence. Moreover, the vitamin release was dramatically diminished following acidification, heating, as well as storage period when the protein-polysaccharide conjugates

were applied as an emulsifier, resulted in the formation of a stable interfacial layer presented by the sodium caseinate-dextran system. This system could be effectual for the development of functional food products to alleviate obesity through decreasing stomach emptying rate and energy uptake. Besides, the superior resistivity of Maillard conjugates vs. enzymatic digestion in the upper parts of the gastrointestinal tract (stomach or small intestine) renders them excellent candidates for engineering colon-specific vehicles to avert/treat bowel ailments. In another study, [Comunian et al. \(2013\)](#) employed an emulsion system stabilized by gelatin-gum arabic coacervates to encapsulate anti-oxidant ascorbic acid with high encapsulation efficiency (approximately 98%), great physicochemical stability, controlled release upon specific circumstances, and potential of masking its acidic taste. [Chapeau et al. \(2016\)](#) utilized a spontaneous co-assembly of whey proteins (i.e., β -lactoglobulin and lactoferrin) as an effective (bio)vehicle for water-soluble vitamin B₉. The authors revealed the useful potentialities of such co-assembly for developing functional food products, proposing promoted health benefits, yet without applying non-food additives.

Essential Oils and Flavors

In a study from [Weinbreck et al. \(2004a,b,c\)](#), bioactive flavors and oils i.e., lemon, sunflower oil, and orange oil have been successfully encapsulated within gum arabic-whey protein coacervate complexes assembled at $\sim$ pH 4.0 with a loading capacity of more than 80%. The release properties of the flavored microcapsules in the model food system (Gouda cheese) demonstrated that the large complexes had the stronger release mechanism. Moreover, the covalently cross-linked particles exhibited the lowest release manner, which was probably related to the tough dense structure of the wall material and thus the difficulty of its breaking by chewing. In another study, the encapsulation of sweet orange oil in electrostatic complexes comprised of gum arabic-soybean protein isolate was potentially performed at a protein: polysaccharide ratio of 1:1 and pH $\sim$ 4.0 with encapsulation yield and encapsulation efficiency of around 90% and 80%, respectively ([Jun-xia et al., 2011](#)). Nevertheless, enhancing the bioactive content (20%–70%) diminished encapsulation yields/efficiencies and considerably. [Ocak \(2012\)](#) exploited an electrostatic complex of collagen hydrolysate-chitosan cross-linked with glutaraldehyde to entrap lavender oil and pointed out the high efficiency of both chitosan and crosslinker concentrations on release manner and encapsulation efficiency of the system. [Table 3](#) summaries some of the electrostatic biopolymer complexes utilized for micro/nanoencapsulation of essential oils and flavors.

In a study conducted by [Yang et al. \(2015a,b\)](#), the applicability of Millard reaction products based on soy protein isolate-soy soluble polysaccharide conjugates was investigated in stabilizing citral-loaded O/W emulsion. Upon thermal processing, storage period, and even in-vitro, the prepared emulsions exhibited a superior physical stability as compared to those formulated by the protein or polysaccharide solely. This was mainly as a result of potent emulsifying capability of protein and the steric stabilizing ability of polysaccharide moiety of the conjugate system, preventing droplets coalescence and promoting physical stability of the vehicle. The designed emulsions retained about 70% of the hydrophobic citral after 2 h in in-vitro gastric condition; whereas the bioactive citral released almost completely following 4 h in simulated intestinal phase.

Functional Oils and Essential Fatty Acids

By virtue of the health-benefiting effects of functional oils, there has been a tremendous increase in development of essential fatty acids (particularly ω -3-fatty acids) comprising food products, over the past several decades. Utilizing protein-polysaccharide complexes and conjugates, as protective carrier matrices, is an effective platform applied for O₂-sensitive oils. In this line, [Pham et al. \(2020\)](#) investigated the potential of flaxseed polyphenol-adducted flaxseed protein isolate-flaxseed gum coacervates to entrap flaxseed oil, where the protein was covalently adducted with hydroxytyrosol/polyphenol. The secondary configuration of the protein isolate was mainly comprised of β -sheet units, even more so after protein-polyphenol covalent conjugation. In comparison with the pure protein and protein-polyphenol adducts, coacervates formulated by flaxseed protein isolate-flaxseed gum, gum-protein-polyphenol, and gum-protein-hydroxytyrosol possessed notably lower β -sheet contents and higher random coil, indicating the less ordered structure of the developed coacervates. The produced microcapsules showed irregular-shaped structure with a wrinkled surface morphology at optimum pH of $\sim$ 4.6 and the protein-to-gum ratio of 6.0 ([Fig. 2\(A–C\)](#)). Coacervates fabricated by gum-protein-hydroxytyrosol showed the highest microencapsulation efficiency and the lowest surface oil of $\sim$ 95% and 1% w/w, respectively. However, the polyphenol-containing coacervates revealed the highest oxidative stability. [Gomez-Estaca et al. \(2016\)](#) displayed that the incorporation of a bioactive oil rich in ω -3 fatty acids within gum arabic/cashew gum-gelatin coacervates could increase the oxidative resistance of the loaded oil. The authors demonstrated that the cross-linked oil-loaded gelatin-gum arabic matrix maintained more stable oxidatively following crosslinking (sinapic acid/transglutaminase). However, there was no discrepancies between the oxidative stability of cross-linked gelatin-cashew gum and non-cross linked counterpart ([Gomez-Estaca et al., 2016](#)). [Liu et al. \(2010\)](#) reported that the oxidative sustainability of the ω -3 fatty acid containing flax seed oil remarkably improved upon its embedment into gelatin-gum arabic capsules ([Liu et al., 2010](#)).

Other Compounds

Intriguingly and with high relevance to (bio)functional food products, protein-polysaccharide systems have exhibited great potential to mask the unpleasant taste/flavor of various bioactive molecules ([Mendanha et al., 2009](#)). More recently, [Zeeb et al. \(2018\)](#)

Table 3 Some examples about the micro- or nanoencapsulation of essential oils and flavors using electrostatic protein-polysaccharide systems

Carrier matrix	Bioactive molecule	Comments	Reference
Flaxseed protein isolate-flaxseed gum complexes	Flaxseed oil	● Production of polyphenol-adducted protein-gum coacervates for encapsulation of the bioactive flaxseed oil. ● About 66%–80% and 5%–17% release of the entrapped oil in intestinal and gastric phases, respectively. ● The reduction of protein degradation in the intestinal stage following the polyphenol adduction. ● The highest (80%) and lowest (66.3%) oil release for gum-protein-hydroxytyrosol and gum-protein-polyphenol, respectively. ● The polyphenol-adducted coacervates was introduced as an efficient carrier agent for successful delivery of the payload to intestinal stage.	Pham <i>et al.</i> (2021)
Gelatin-gum arabic complexes	Garlic oil	● The highest loading efficiency and the maximum bioactive encapsulation yield of gelatin (type A/B)-gum at pH = 3.5 and 4.5, respectively. ● Generation of spherical-shaped coacervates with smooth topography and controlled bioactive release. ● The potential shield of bioactive-loaded coacervates from primary and secondary oxidation for 12 days at 45°C.	Siow and Ong (2013)
Chia seed protein-chia seed gum complexes	Chia seed oil	● The High lipolysis and release of chia seed oil from the spray-dried coacervates was highly dependent to shell composition. ● The highest release of the bioactive oil in gastric phase due to the hydrolysis of chia seed protein isolate and thus erosion of carrier matrix. ● The oil hydrolysis at intestinal phase following the action of pancreatic lipase. ● The oil hydrolysis of ~100% and 60% for free and encapsulated oil, respectively.	Timilsena <i>et al.</i> (2017)
Gelatin-gum arabic complexes	Bake flavor oil	● Effectiveness of both polyion concentration and homogenization rate on complex morphology, size distribution, and even the release mechanism of the flavor during heating. ● Fabrication of uni-vesicular structures through lower homogenization rates that released almost all of the loaded bioactive at 100°C or higher temperatures. ● Production of multi-vesicular bodies by high homogenization rates with a considerably lower release rate as compared to uni-vesicular ones. ● Improvement of the frozen baked foods by temperature-dependent release of the loaded flavors.	Yeo <i>et al.</i> (2005b)
Gelatin-gum arabic complexes	Allyl isothiocyanate	● Promoted sustained release of the payload following the tannic acid cross-linking. ● High encapsulation efficiency of the coacervate microcapsules.	Zhang <i>et al.</i> (2011)
Gelatin-gum arabic complexes	Xylitol	● Successful encapsulation of xylitol via a double emulsion approach followed by complex coacervation. ● Application of xylitol-loaded capsules in food products to extend their sweetness. ● Production of low soluble and small size complexes. ● Development of complex systems of high encapsulation efficiency for a hydrophilic payload.	Santos <i>et al.</i> (2015)
Soy protein isolate-Chitosan complexes	Algal oil	● Entropy/enthalpy dependency of the coacervation process. ● Viscoelastic solid behavior and gel-like structure of coacervates with high encapsulation efficiency. ● Improved oxidation stability of the bioactive oil following the encapsulation within coacervates.	Yuan <i>et al.</i> (2017)
Gelatin- Polyphosphate complexes	Fish oil	● Equivalent bioavailability of the bioactive oil following its incorporation within coacervate or soft-gel microcapsules.	Barrow <i>et al.</i> (2009)

(Continued)

Table 3 Continued

Carrier matrix	Bioactive molecule	Comments	Reference
Chitosan-xanthan/pectin complexes	Palm oil	- Superior yield, high encapsulation efficiency, and the unique release manner of lyophilized samples. - The best in vivo release of the bioactive was obtained for chitosan-pectin complexes. - The best release mechanism of the bioactive was observed in the yogurt for chitosan-xanthan micro-capsules.	Rutz <i>et al.</i> (2017)
Gelatin – Sodium Hexametaphosphate complexes	Tuna oil	- High encapsulation efficiency and yield of tuna oil after encapsulation. - Superior oxidative stability of the bioactive oil as compared to free oil.	Wang <i>et al.</i> (2014)
Cold water fish gelatine- gum arabic complexes	Sunflower oil	- Production of homogeneous protein-polysaccharide micro-capsules at room temperature. - Successful cross-linking of the coacervate shell via glutaraldehyde. - Possibility of continuous fabrication of capsules with controlled size and significantly low energy.	Piacentini <i>et al.</i> (2013)
Maillard conjugates of Glycated caseinate-glucose/ glucose sirup/ dextran	Fish oils	- Fabrication of conjugates via dry or wet heating reaction. - The improved oxidative stability of the bioactive loaded in caseinate-glucose sirup prepared through wet heating, resulted in the production of the redox active elements. - Higher stability of oil-loaded caseinate-glucose conjugate in comparison with the bioactive-containing caseinate-glucose sirup. - The increased stability to oxidation owing to the antioxidant property and emulsification capacity of protein-polysaccharide conjugates.	Drusch <i>et al.</i> (2009)
Whey protein isolate-maltodextrin Maillard conjugates	Eugenol	- Maillard conjugation using an emulsion-evaporation method. - Formation of heat stable dispersions at pH 3.0, 7.0, and even 5.0. - Enhanced both encapsulation and dispersion features at lower protein to polysaccharide ratios.	Shah <i>et al.</i> (2012a)
Whey protein isolate-maltodextrin Maillard conjugates	Lipophilic anti-microbial thymol	- Improved dispersibility, transparency, as well as thermal resistance of the nano-dispersions even at high bioactive content and pH ranges close to pI of the protein. - Promoted heat stability and solubility of the protein following the glycation process, as a result of steric stabilization induced by the polysaccharide moiety. - Encapsulation efficiency and mass yield of 35.7 g/100 g and 82.7 g/100 g, respectively.	Shah <i>et al.</i> (2012b)

successfully improved the perceived sensorial acceptance of novel *plant proteins* (i.e., pea and potato proteins) through the complexation with apple pectin (Zeeb *et al.*, 2018).

The significance of *probiotic bacteria* and their live delivery in vivo have also gained substantial attention nowadays. For example, co-encapsulation and assessment of probiotic bacteria (*Lactobacillus casei* 431) and ω -3 fatty acids (tuna oil) enclosed in complex coacervates of gum arabic-whey protein isolate was evaluated by Eratte *et al.* (2015). The authors illustrated that the viability of the encapsulated probiotic and the oxidative stability of ω -3 fatty acids significantly enhanced upon encapsulation within the protein-gum complex system. Microencapsulation of other probiotic bacteria e.g., *Lactobacillus paracasei* and *Lactobacillus paraplantarum* within whey protein isolate-gum arabic coacervates have also been reported previously (Bosnea *et al.*, 2017, 2014). In another study, *Lactobacillus rhamnosus* was entrapped into Maillard conjugates of whey protein-isomaltooligosaccharide by using cold gelation within an emulsion system and its survival was investigated following in vitro digestion (Liu *et al.*, 2016). The fabricated microspheres represented high encapsulation efficiency of ~89%, which was relevant to the hydrophilic-hydrophobic balanced glycoprotein in protein-polysaccharide conjugates and thus lower interfacial tension in system. Moreover, the buffer capacity of the protein molecules in firm network developed by conjugates, considerably decreased the diffusion rate of acid into the microspheres and increased the pH-senility of the probiotic.

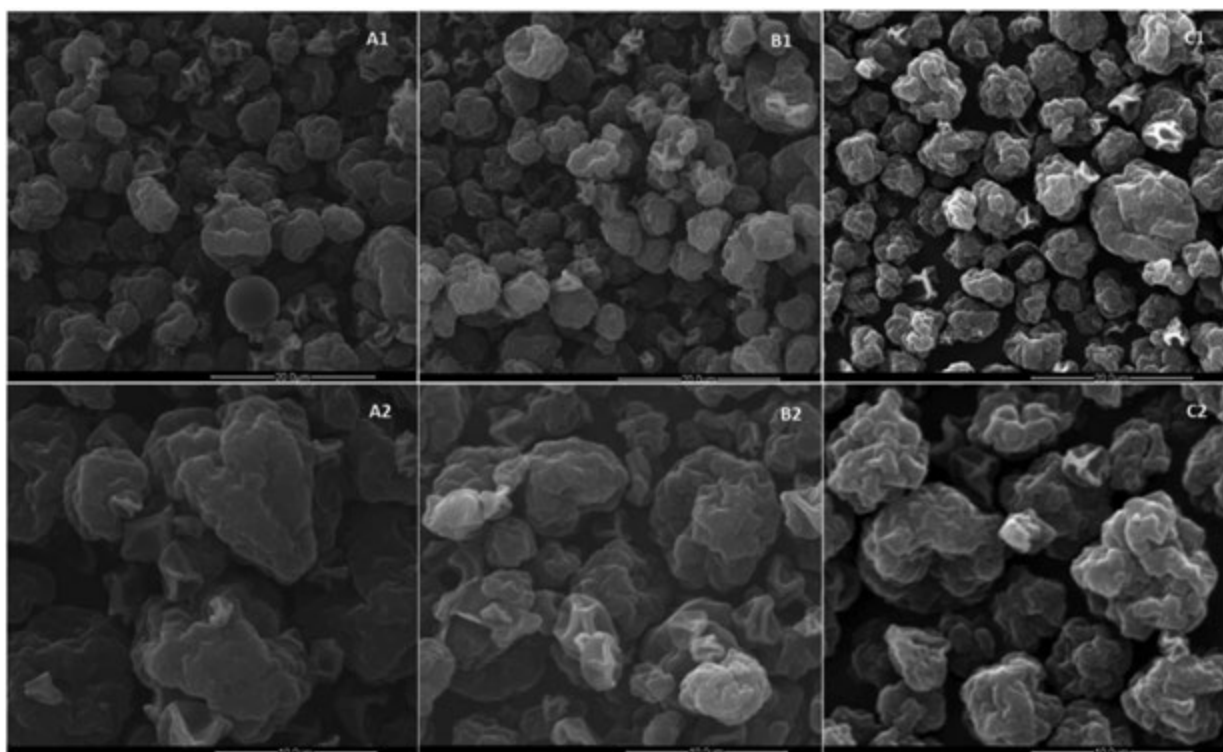


Fig. 2 SEM micrographs of spray-dried capsules generated by flaxseed protein isolate-flaxseed gum (A), polyphenol-protein-gum (B), and gum-protein-hydroxytyrosol coacervates (subscripts 1 and 2 refer to scale bars of 20 and 10 μm , respectively). Reproduced from Pham, L.B., Wang, B., Zisu, B., Truong, T., Adhikari, B., 2020. Microencapsulation of flaxseed oil using polyphenol-adducted flaxseed protein isolate-flaxseed gum complex coacervates. *Food Hydrocolloids* 107, 105944. Available at: <https://doi.org/10.1016/j.foodhyd.2020.105944>.

Conclusion

By virtue of their unique attributes, the covalent and electrostatic protein-polysaccharide based vehicles are efficient delivery systems to nano/micro-encapsulate, shield, as well as deliver a vast variety of bioactive molecules in the food and medical/pharmaceutical sectors. This article has offered an overview of electrostatic complex or Maillard conjugate-stabilized vehicles, in which the protein-polysaccharide system offers a continuous and thick cover around the payload, lowering its degradability upon processing, storage time, utilization, as well as gastric transition. Therefore, the electrostatic complexes and Maillard conjugates of proteins and polysaccharides could be utilized as promising delivery systems to promote bioavailability and (bio)stability of nutraceuticals and formulate multi-functional products for the food/medicinal implementations. Nevertheless, more research studies are still required to characterize the protein-polysaccharide electrostatic complexes and Maillard reaction products to develop a biopolymer system of high functionality for designing a nutraceutical delivery system *in vitro/ in vivo*. It is also useful to note that the lower digestion rate of Maillard products can be useful in reducing the gastric discharging rate and the perceived energy from the foods, useful in treating the obesity patients. Besides, it seems that more *in vitro/ in vivo* investigations are required to consistently assess the efficiency of the covalent and electrostatic protein-polysaccharide based vehicles.

References

- Abaee, A., Mohammadian, M., Jafari, S.M., 2017. Whey and soy protein-based hydrogels and nano-hydrogels as bioactive delivery systems. *Trends in Food Science & Technology* 70, 69–81. <https://doi.org/10.1016/j.tifs.2017.10.011>.
- Aditya, N.P., Espinosa, Y.G., Norton, I.T., 2017. Encapsulation systems for the delivery of hydrophilic nutraceuticals: Food application. *Biotechnology Advances* 35 (4), 450–457.
- Akhtar, M., Ding, R., 2017. Covalently cross-linked proteins & polysaccharides: Formation, characterisation and potential applications. *Current Opinion in Colloid & Interface Science* 28, 31–36. <https://doi.org/10.1016/j.cocis.2017.01.002>.
- Amara, C.B., Kim, L., Oulahal, N., Degraeve, P., Gharsallaoui, A., 2017. Using complexation for the microencapsulation of nisin in biopolymer matrices by spray-drying. *Food Chemistry* 236, 32–40.
- Assadpour, E., Jafari, S.M., 2018. A systematic review on nanoencapsulation of food bioactive ingredients and nutraceuticals by various nanocarriers. *Critical Reviews in Food Science and Nutrition*. 1–47.
- Assadpour, E., Jafari, S.M., 2019. Chapter 3 – Nanoencapsulation: Techniques and developments for food applications. In: López Rubio, A., Fabra Rovira, M.J., Martínez Sanz, M., Gómez-Mascaraque, L.G. (Eds.), *Nanomaterials for Food Applications*. Elsevier, pp. 35–61. <https://doi.org/10.1016/B978-0-12-814130-4.00003-8>.

- Assadpour, E., Jafari, S.-M., Maghsoudlou, Y., 2017. Evaluation of folic acid release from spray dried powder particles of pectin-whey protein nano-capsules. *International Journal of Biological Macromolecules* 95, 238–247. <https://doi.org/10.1016/j.ijbiomac.2016.11.023>.
- Assadpour, E., Rostamabadi, H., Jafari, S.M., 2020. Chapter One – Introduction to characterization of nanoencapsulated food ingredients. In: Jafari, S.M. (Ed.), *Characterization of Nanoencapsulated Food Ingredients* 4. Academic Press, pp. 1–50. <https://doi.org/10.1016/B978-0-12-815667-4.00001-8>.
- Aylanc, V., Ertosun, S., Akyuz, L., *et al.*, 2020. Natural β -chitin-protein complex film obtained from waste razor shells for transdermal capsaicin carrier. *International Journal of Biological Macromolecules* 155, 508–515. <https://doi.org/10.1016/j.ijbiomac.2020.03.232>.
- Barrow, C.J., Nolan, C., Holub, B.J., 2009. Bioequivalence of encapsulated and microencapsulated fish-oil supplementation. *Journal of Functional Foods* 1 (1), 38–43. <https://doi.org/10.1016/j.jff.2008.09.006>.
- Bolhassani, A., Javanad, S., Saleh, T., *et al.*, 2014. Polymeric nanoparticles. *Human Vaccines & Immunotherapeutics* 10 (2), 321–332. <https://doi.org/10.4161/hv.26796>.
- Boostani, S., Jafari, S.M., 2020. Chapter Two – Controlled release of nanoencapsulated food ingredients. In: Jafari, S.M. (Ed.), *Release and Bioavailability of Nanoencapsulated Food Ingredients*. Elsevier, pp. 27–78.
- Bosnea, L.A., Moschakis, T., Biliaderis, C.G., 2017. Microencapsulated cells of *Lactobacillus paracasei* subsp. *Paracasei* in biopolymer complex coacervates and their function in a yogurt matrix. *Food & Function* 8 (2), 554–562. <https://doi.org/10.1039/C6FO01019A>.
- Bosnea, L.A., Moschakis, T., Biliaderis, C.G., 2014. Complex coacervation as a novel microencapsulation technique to improve viability of probiotics under different stresses. *Food and Bioprocess Technology* 7 (10), 2767–2781.
- Campos, E.V.R., de Oliveira, J.L., Fraceto, L.F., Singh, B., 2015. Polysaccharides as safer release systems for agrochemicals. *Agronomy for Sustainable Development* 35 (1), 47–66.
- Chapeau, A.-L., Tavares, G.M., Hamon, P., *et al.*, 2016. Spontaneous co-assembly of lactoferrin and β -lactoglobulin as a promising biocarrier for vitamin B9. *Food Hydrocolloids* 57, 280–290. <https://doi.org/10.1016/j.foodhyd.2016.02.003>.
- Chen, B., Guo, Z., Miao, S., *et al.*, 2018. Preparation and characterization of lotus seed starch-fatty acid complexes formed by microfluidization. *Journal of Food Engineering* 237, 52–59.
- Chen, L., Remondetto, G.E., Subirade, M., 2006. Food protein-based materials as nutraceutical delivery systems. *Trends in Food Science & Technology* 17 (5), 272–283.
- Chourpa, I., Ducel, V., Richard, J., Dubois, P., Boury, F., 2006. Conformational modifications of α gliadin and globulin proteins upon complex coacervates formation with gum arabic as studied by Raman microspectroscopy. *Biomacromolecules* 7 (9), 2616–2623.
- Clarke, A.W., Arnsperg, E.C., Mithieux, S.M., *et al.*, 2006. Tropoelastin massively associates during coacervation to form quantized protein spheres. *Biochemistry* 45 (33), 9989–9996. <https://doi.org/10.1021/bi0610092>.
- Comunian, T.A., Thomazini, M., Alves, A.J.G., *et al.*, 2013. Microencapsulation of ascorbic acid by complex coacervation: Protection and controlled release. *Food Research International* 52 (1), 373–379. <https://doi.org/10.1016/j.foodres.2013.03.028>.
- Cooper, C.L., Dubin, P.L., Kayitmazer, A.B., Turksen, S., 2005. Polyelectrolyte–protein complexes. *Current Opinion in Colloid & Interface Science* 10 (1), 52–78. <https://doi.org/10.1016/j.cocis.2005.05.007>.
- Croguennec, T., Tavares, G.M., Bouhallab, S., 2017. Heteroprotein complex coacervation: A generic process. *Advances in Colloid and Interface Science* 239, 115–126. <https://doi.org/10.1016/j.cis.2016.06.009>.
- Dai, L., Wei, Y., Sun, C., *et al.*, 2018. Development of protein-polysaccharide-surfactant ternary complex particles as delivery vehicles for curcumin. *Food Hydrocolloids* 85, 75–85. <https://doi.org/10.1016/j.foodhyd.2018.06.052>.
- Dai, R.Y., You, S.Y., Lu, L.M., *et al.*, 2017. High blades spreadability of chlorpyrifos microcapsules prepared with polysiloxane sodium carboxylate/sodium carboxymethylcellulose/gelatin via complex coacervation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 530, 13–19. <https://doi.org/10.1016/j.colsurfa.2017.06.057>.
- Damodaran, S., 2005. Protein stabilization of emulsions and foams. *Journal of Food Science* 70 (3), R54–R66. <https://doi.org/10.1111/j.1365-2621.2005.tb07150.x>.
- De Fenoyl, L., Hirel, D., Perez, E., *et al.*, 2018. Interfacial activity and emulsifying behaviour of inclusion complexes between helical polysaccharides and flavouring molecules resulting from non-covalent interactions. *Food Research International* 105, 801–811.
- de Oliveira, F.C., Dos Reis Coimbra, J.S., de Oliveira, E.B., Zúñiga, A.D.G., Garcia Rojas, E.E., 2016. Food protein-polysaccharide conjugates obtained via the Maillard reaction: A review. *Critical Reviews in Food Science and Nutrition* 56 (7), 1108–1125.
- de Oliveira, W.Q., Wurlitzer, N.J., de Oliveira Araújo, A.W., *et al.*, 2020. Complex coacervates of cashew gum and gelatin as carriers of green coffee oil: The effect of microcapsule application on the rheological and sensorial quality of a fruit juice. *Food Research International* 131, 109047.
- Devi, N., Maji, T.K., 2011. Study of complex coacervation of gelatin A with sodium carboxymethyl cellulose: Microencapsulation of neem (*Azadirachta indica* A. Juss.) seed oil (NSO). *International Journal of Polymeric Materials* 60 (13), 1091–1105.
- Devi, N., Kakati, D.K., 2013. Smart porous microparticles based on gelatin/sodium alginate polyelectrolyte complex. *Journal of Food Engineering* 117 (2), 193–204.
- Dickinson, E., 2010. Flocculation of protein-stabilized oil-in-water emulsions. *Colloids and Surfaces B: Biointerfaces* 81 (1), 130–140. <https://doi.org/10.1016/j.colsurfb.2010.06.033>.
- Dima, C., Assadpour, E., Dima, S., Jafari, S.M., 2020. Bioactive-loaded nanocarriers for functional foods: From designing to bioavailability. *Current Opinion in Food Science* 33, 21–29. <https://doi.org/10.1016/j.cofs.2019.11.006>.
- Dong, X., Du, S., Deng, Q., *et al.*, 2020. Study on the antioxidant activity and emulsifying properties of flaxseed gum-whey protein isolate conjugates prepared by Maillard reaction. *International Journal of Biological Macromolecules* 153, 1157–1164. <https://doi.org/10.1016/j.ijbiomac.2019.10.245>.
- Doublier, J.-L., Garnier, C., Renard, D., Sanchez, C., 2000. Protein–polysaccharide interactions. *Current Opinion in Colloid & Interface Science* 5 (3), 202–214. [https://doi.org/10.1016/S1359-0294\(00\)00054-6](https://doi.org/10.1016/S1359-0294(00)00054-6).
- Drusch, S., Berg, S., Scampicchio, M., *et al.*, 2009. Role of glycosylated caseinate in stabilisation of microencapsulated lipophilic functional ingredients. *Food Hydrocolloids* 23 (3), 942–948.
- Du, J., Sun, R., Zhang, S., *et al.*, 2004. Novel polyelectrolyte carboxymethyl konjac glucomannan–chitosan nanoparticles for drug delivery. *Macromolecular Rapid Communications* 25 (9), 954–958.
- Ducel, V., Pouliquen, D., Richard, J., Boury, F., 2008. ¹H NMR relaxation studies of protein–polysaccharide mixtures. *International Journal of Biological Macromolecules* 43 (4), 359–366.
- Elzoghby, A.O., El-Fotoh, W.S.A., Elgindy, N.A., 2011. Casein-based formulations as promising controlled release drug delivery systems. *Journal of Controlled Release* 153 (3), 206–216.
- Elzoghby, A.O., Samy, W.M., Elgindy, N.A., 2012. Albumin-based nanoparticles as potential controlled release drug delivery systems. *Journal of Controlled Release* 157 (2), 168–182.
- Eratte, D., McKnight, S., Gengenbach, T.R., *et al.*, 2015. Co-encapsulation and characterisation of omega-3 fatty acids and probiotic bacteria in whey protein isolate–gum Arabic complex coacervates. *Journal of Functional Foods* 19, 882–892.
- Esfahani, R., Jafari, S.M., Jafarpour, A., Dehnad, D., 2019. Loading of fish oil into nanocarriers prepared through gelatin–gum Arabic complexation. *Food Hydrocolloids* 90, 291–298. <https://doi.org/10.1016/j.foodhyd.2018.12.044>.
- Esfarjani, A.F., Jafari, S.M., 2016. Biopolymer nano-particles and natural nano-carriers for nano-encapsulation of phenolic compounds. *Colloids and Surfaces B: Biointerfaces* 146, 532–543.
- Falsafi, S.R., Maghsoudlou, Y., Rostamabadi, H., *et al.*, 2019. Preparation of physically modified oat starch with different sonication treatments. *Food Hydrocolloids* 89, 311–320.

- Falsafi, S.R., Rostamabadi, H., Assadpour, E., Jafari, S.M., 2020a. Morphology and microstructural analysis of bioactive-loaded micro/nanocarriers via microscopy techniques; CLSM/SEM/TEM/AFM. *Advances in Colloid and Interface Science* 280, 102166. <https://doi.org/10.1016/j.cis.2020.102166>.
- Falsafi, S.R., Rostamabadi, H., Jafari, S.M., 2020b. Chapter Nine – X-ray diffraction (XRD) of nanoencapsulated food ingredients. In: Jafari, S.M. (Ed.), *Characterization of Nanoencapsulated Food Ingredients* 4. Academic Press, pp. 271–293. <https://doi.org/10.1016/B978-0-12-815566-7.4.00009-2>.
- Falsafi, S.R., Maghsoudlou, Y., Alalami, M., Jafari, S.M., Raeisi, M., 2018. Physicochemical and morphological properties of resistant starch type 4 prepared under ultrasound and conventional conditions and their in-vitro and in-vivo digestibilities. *Ultrasonics Sonochemistry* 53.
- Fan, Y., Yi, J., Zhang, Y., Yokoyama, W., 2018. Fabrication of curcumin-loaded bovine serum albumin (BSA)-dextran nanoparticles and the cellular antioxidant activity. *Food Chemistry* 239, 1210–1218. <https://doi.org/10.1016/j.foodchem.2017.07.075>.
- Fechner, A., Knoth, A., Scherze, I., Muschliolik, G., 2007. Stability and release properties of double-emulsions stabilised by caseinate–dextran conjugates. *Food Hydrocolloids* 21 (5), 943–952. <https://doi.org/10.1016/j.foodhyd.2006.10.021>.
- Gaber, M., Mabrouk, M.T., Freag, M.S., *et al.*, 2018. Protein-polysaccharide nanohybrids: Hybridization techniques and drug delivery applications. *European Journal of Pharmaceutics and Biopharmaceutics* 133, 42–62.
- García-Herraz, A., Leiva-García, R., Cañigral-Ortiz, A., Silvestre, F.J., García-Antón, J., 2012. Confocal laser scanning microscopy for the study of the morphological changes of the postextraction sites. *Microscopy Research and Technique* 75 (4), 513–519.
- Gentile, L., 2020. Protein–polysaccharide interactions and aggregates in food formulations. *Current Opinion in Colloid & Interface Science* 48, 18–27. <https://doi.org/10.1016/j.cocis.2020.03.002>.
- George, D., Maheswari, P.U., Begum, K.M.M.S., 2020. Chitosan-cellulose hydrogel conjugated with L-histidine and zinc oxide nanoparticles for sustained drug delivery: Kinetics and in-vitro biological studies. *Carbohydrate Polymers* 236, 116101. <https://doi.org/10.1016/j.carbpol.2020.116101>.
- Ghasemi, S., Jafari, S.M., Assadpour, E., Khomeiri, M., 2018. Nanoencapsulation of d-limonene within nanocarriers produced by pectin-whey protein complexes. *Food Hydrocolloids* 77, 152–162.
- Girard, M., Turgeon, S.L., Gauthier, S.F., 2003. Quantification of the interactions between β -lactoglobulin and pectin through capillary electrophoresis analysis. *Journal of Agricultural and Food Chemistry* 51 (20), 6043–6049.
- Gomez-Estaca, J., Comunian, T.A., Montero, P., Ferro-Furtado, R., Favaro-Trindade, C.S., 2016. Encapsulation of an astaxanthin-containing lipid extract from shrimp waste by complex coacervation using a novel gelatin–cashew gum complex. *Food Hydrocolloids* 61, 155–162. <https://doi.org/10.1016/j.foodhyd.2016.05.005>.
- Gumus, C.E., Davidov-Pardo, G., McClements, D.J., 2016. Lutein-enriched emulsion-based delivery systems: Impact of Maillard conjugation on physicochemical stability and gastrointestinal fate. *Food Hydrocolloids* 60, 38–49.
- Gupta, P., Nayak, K.K., 2015. Characteristics of protein-based biopolymer and its application. *Polymer Engineering & Science* 55 (3), 485–498.
- Hifumi, H., Ewing, A.V., Kazarian, S.G., 2016. ATR-FTIR spectroscopic imaging to study the drying and dissolution of pharmaceutical polymer-based films. *International Journal of Pharmaceutics* 515 (1), 57–68. <https://doi.org/10.1016/j.ijpharm.2016.09.085>.
- Hsu, C.-Y., Wang, P.-W., Alalaiwe, A., Lin, Z.-C., Fang, J.-Y., 2019. Use of lipid nanocarriers to improve oral delivery of vitamins. *Nutrients* 11 (1), 68.
- Jacob, J., Haponiuk, J.T., Thomas, S., Gopi, S., 2018. Biopolymer based nanomaterials in drug delivery systems: A review. *Materials Today Chemistry* 9, 43–55.
- Jafari, S.M., McClements, D.J., 2017. Nanotechnology approaches for increasing nutrient bioavailability. *Advances in Food and Nutrition Research* 81, 1–30.
- Jain, A., Thakur, D., Ghoshal, G., Kataré, O.P., Shivhare, U.S., 2016. Characterization of microcapsulated β -carotene formed by complex coacervation using casein and gum tragacanth. *International Journal of Biological Macromolecules* 87, 101–113. <https://doi.org/10.1016/j.ijbiomac.2016.01.117>.
- Joye, I.J., McClements, D.J., 2014. Biopolymer-based nanoparticles and microparticles: Fabrication, characterization, and application. *Current Opinion in Colloid & Interface Science* 19 (5), 417–427.
- Jun-xia, X., Hai-yan, Y., Jian, Y., 2011. Microencapsulation of sweet orange oil by complex coacervation with soybean protein isolate/gum Arabic. *Food Chemistry* 125 (4), 1267–1272. <https://doi.org/10.1016/j.foodchem.2010.10.063>.
- Kayitmazer, A.B., Seeman, D., Minsky, B.B., Dubin, P.L., Xu, Y., 2013. Protein–polyelectrolyte interactions. *Soft Matter* 9 (9), 2553–2583. <https://doi.org/10.1039/C2SM27002A>.
- Kim, S., Huang, J., Lee, Y., *et al.*, 2016. Complexation and coacervation of like-charged polyelectrolytes inspired by mussels. *Proceedings of the National Academy of Sciences of the United States of America* 113 (7), E847–E853.
- Kim, S., Shin, W.-S., 2020. Formation of a novel coating material containing lutein and zeaxanthin via a Maillard reaction between bovine serum albumin and fucoidan. *Food Chemistry* 343, 128437. <https://doi.org/10.1016/j.foodchem.2020.128437>.
- Kong, X.Z., Gu, X., Zhu, X., Zhang, Z., 2009. Spreadable dispersion of insect sex pheromone capsules, preparation via complex coacervation and release control of the encapsulated pheromone component molecule. *Biomedical Microdevices* 11 (1), 275–285. <https://doi.org/10.1007/s10544-008-9234-z>.
- Koupantsis, T., Pavlidou, E., Paraskevopoulou, A., 2014. Flavour encapsulation in milk proteins–CMC coacervate-type complexes. *Food Hydrocolloids* 37, 134–142.
- Laneuville, S.L., Turgeon, S.L., Sanchez, C., Paquin, P., 2006. Gelation of native β -Lactoglobulin induced by electrostatic attractive interaction with xanthan gum. *Langmuir* 22 (17), 7351–7357. <https://doi.org/10.1021/la060149+>.
- Lee, J.W., Park, J.H., Robinson, J.R., 2000. Bioadhesive-based dosage forms: The next generation. *Journal of Pharmaceutical Sciences* 89 (7), 850–866.
- Siow, L.-F., Ong, C.-S., 2013. Effect of pH on garlic oil encapsulation by complex coacervation. *Journal of Food Processing and Technology* 4 (1). <https://www.cabdirect.org/cabdirect/abstract/20133129475>.
- Li, H., Yang, H., Li, P., *et al.*, 2020. Maillard reaction products with furan ring, like furosine, cause kidney injury through triggering ferroptosis pathway. *Food Chemistry* 319, 126368. <https://doi.org/10.1016/j.foodchem.2020.126368>.
- Li, Z., Gu, L., 2014. Fabrication of self-assembled (–)-epigallocatechin gallate (EGCG) ovalbumin–dextran conjugate nanoparticles and their transport across monolayers of human intestinal epithelial Caco-2 cells. *Journal of Agricultural and Food Chemistry* 62 (6), 1301–1309. <https://doi.org/10.1021/jf404621f>.
- Liu, L., Li, X., Zhu, Y., *et al.*, 2016. Effect of microencapsulation with Maillard reaction products of whey proteins and isomaltotriigosaccharide on the survival of *Lactobacillus rhamnosus*. *LWT* 73, 37–43.
- Liu, S., Low, N.H., Nickerson, M.T., 2010. Entrapment of flaxseed oil within gelatin–gum arabic capsules. *Journal of the American Oil Chemists' Society* 87 (7), 809–815.
- Liu, Z., Jiao, Y., Liu, F., Zhang, Z., 2007. Heparin/chitosan nanoparticle carriers prepared by polyelectrolyte complexation. In: Anderson, J.M., Kent Leach, J. (Eds.), *Journal of Biomedical Materials Research Part A* 83. Wiley, pp. 806–812.
- Liu, Z., Jiao, Y., Wang, Y., Zhou, C., Zhang, Z., 2008. Polysaccharides-based nanoparticles as drug delivery systems. *Advanced Drug Delivery Reviews* 60 (15), 1650–1662.
- Lopes, N.A., Pinilla, C.M.B., Brandelli, A., 2019. Antimicrobial activity of lysozyme–nisin co-encapsulated in liposomes coated with polysaccharides. *Food Hydrocolloids* 93, 1–9.
- Mekhloufi, G., Sanchez, C., Renard, D., Guillemin, S., Hardy, J., 2005. PH-induced structural transitions during complexation and coacervation of β -lactoglobulin and acacia gum. *Langmuir* 21 (1), 386–394.
- Mendanha, D.V., Molina Ortiz, S.E., Favaro-Trindade, C.S., *et al.*, 2009. Microencapsulation of casein hydrolysate by complex coacervation with SPI/pectin. *Food Research International* 42 (8), 1099–1104. <https://doi.org/10.1016/j.foodres.2009.05.007>.
- Michalska, A., Honke, J., Łysiak, G., Andlauer, W., 2016. Effect of drying parameters on the formation of early and intermediate stage products of the Maillard reaction in different plum (*Prunus domestica* L.) cultivars. *LWT - Food Science and Technology* 65, 932–938. <https://doi.org/10.1016/j.lwt.2015.09.015>.
- Nigen, M., Croguennec, T., Renard, D., Bouhallab, S., 2007. Temperature affects the supramolecular structures resulting from α -Lactalbumin – Lysozyme interaction. *Biochemistry* 46 (5), 1248–1255. <https://doi.org/10.1021/bi062129c>.
- Nitta, S.K., Numata, K., 2013. Biopolymer-based nanoparticles for drug/gene delivery and tissue engineering. *International Journal of Molecular Sciences* 14 (1), 1629–1654.

- Ocak, B., 2012. Complex coacervation of collagen hydrolysate extracted from leather solid wastes and chitosan for controlled release of lavender oil. *Journal of Environmental Management* 100, 22–28. <https://doi.org/10.1016/j.jenvman.2012.01.026>.
- Park, S.-B., Lih, E., Park, K.-S., Joung, Y.K., Han, D.K., 2017. Biopolymer-based functional composites for medical applications. *Progress in Polymer Science* 68, 77–105.
- Park, S.J., Garcia, C.V., Shin, G.H., Kim, J.T., 2018. Improvement of curcuminoid bioaccessibility from turmeric by a nanostructured lipid carrier system. *Food Chemistry* 251, 51–57.
- Peltonen, L., 2018. Practical guidelines for the characterization and quality control of pure drug nanoparticles and nano-cocrystals in the pharmaceutical industry. *Advanced Drug Delivery Reviews* 131, 101–115. <https://doi.org/10.1016/j.addr.2018.06.009>.
- Pham, L.B., Wang, B., Zisu, B., Truong, T., Adhikari, B., 2020. Microencapsulation of flaxseed oil using polyphenol-adducted flaxseed protein isolate-flaxseed gum complex coacervates. *Food Hydrocolloids* 107, 105944. <https://doi.org/10.1016/j.foodhyd.2020.105944>.
- Pham, L.B., Wang, B., Zisu, B., Truong, T., Adhikari, B., 2021. In-vitro digestion of flaxseed oil encapsulated in phenolic compound adducted flaxseed protein isolate-flaxseed gum complex coacervates. *Food Hydrocolloids* 112, 106325. <https://doi.org/10.1016/j.foodhyd.2020.106325>.
- Piacentini, E., Giorno, L., Dragosavac, M.M., Vladislavjević, G.T., Holdich, R.G., 2013. Microencapsulation of oil droplets using cold water fish gelatine/gum arabic complex coacervation by membrane emulsification. *Food Research International* 53 (1), 362–372.
- Reis, C.P., Neufeld, R.J., Ribeiro, A.J., Veiga, F., 2006. Nanoencapsulation I. Methods for preparation of drug-loaded polymeric nanoparticles. *Nanomedicine: Nanotechnology, Biology and Medicine* 2 (1), 8–21.
- Rostamabadi, H., Falsafi, S.R., Jafari, S.M., 2019a. Nanoencapsulation of carotenoids within lipid-based nanocarriers. *Journal of Controlled Release* 298, 38–67.
- Rostamabadi, H., Falsafi, S.R., Jafari, S.M., 2019b. Nano-helices of amylose for encapsulation of food ingredients. In *Biopolymer Nanostructures for Food Encapsulation Purposes*. Elsevier, pp. 463–491.
- Rostamabadi, H., Falsafi, S.R., Jafari, S.M., 2019c. Starch-based nanocarriers as cutting-edge natural cargos for nutraceutical delivery. *Trends in Food Science & Technology* 88, 397–415.
- Rostamabadi, H., Falsafi, S.R., Jafari, S.M., 2019d. Chapter 15 – Nanostructures of starch for encapsulation of food ingredients. In: Jafari, S.M. (Ed.), *Biopolymer Nanostructures for Food Encapsulation Purposes*. Academic Press, pp. 419–462. <https://doi.org/10.1016/B978-0-12-815663-6.00015-X>.
- Rostamabadi, H., Mahoonak, A.S., Allafchian, A., Ghorbani, M., 2019e. Fabrication of β -carotene loaded glucuronoxylan-based nanostructures through electrohydrodynamic processing. *International Journal of Biological Macromolecules* 139, 773–784.
- Rostamabadi, H., Assadpour, E., Tabarestani, H.S., Falsafi, S.R., Jafari, S.M., 2020a. Electrospinning approach for nanoencapsulation of bioactive compounds; recent advances and innovations. *Trends in Food Science & Technology* 100, 190–209. <https://doi.org/10.1016/j.tifs.2020.04.012>.
- Rostamabadi, H., Falsafi, S.R., Assadpour, E., Jafari, S.M., 2020b. Evaluating the structural properties of bioactive-loaded nanocarriers with modern analytical tools. *Comprehensive Reviews in Food Science and Food Safety* 19, 3266–3322. <https://doi.org/10.1111/1541-4337.12653>.
- Rostamabadi, H., Falsafi, S.R., Jafari, S.M., 2020c. Chapter Two – Transmission electron microscopy (TEM) of nanoencapsulated food ingredients. In: Jafari, S.M. (Ed.), *Characterization of Nanoencapsulated Food Ingredients 4*. Academic Press, pp. 53–82. <https://doi.org/10.1016/B978-0-12-815667-4.00002-X>.
- Rubinstein, A., 2000. Natural polysaccharides as targeting tools of drugs to the human colon. *Drug Development Research* 50 (3–4), 435–439.
- Rutz, J.K., Borges, C.D., Zambiasi, R.C., et al., 2017. Microencapsulation of palm oil by complex coacervation for application in food systems. *Food Chemistry* 220, 59–66. <https://doi.org/10.1016/j.foodchem.2016.09.194>.
- Samant, S.K., Singhal, R.S., Kulkarni, P.R., Rege, D.V., 1993. Protein-polysaccharide interactions: A new approach in food formulations. *International Journal of Food Science & Technology* 28 (6), 547–562. <https://doi.org/10.1111/j.1365-2621.1993.tb01306.x>.
- Santos, M.G., Bozza, F.T., Thomazini, M., Favaro-Trindade, C.S., 2015. Microencapsulation of xylitol by double emulsion followed by complex coacervation. *Food Chemistry* 171, 32–39. <https://doi.org/10.1016/j.foodchem.2014.08.093>.
- Schmidt, I., Cousin, F., Huchon, C., Boué, F., Axelos, M.A., 2009. Spatial structure and composition of polysaccharide – Protein complexes from small angle neutron scattering. *Biomacromolecules* 10 (6), 1346–1357.
- Schmitt, C., Turgeon, S.L., 2011. Protein/polysaccharide complexes and coacervates in food systems. *Advances in Colloid and Interface Science* 167 (1–2), 63–70.
- Schmitt, C., Sanchez, C., Lamprecht, A., et al., 2001. Study of β -lactoglobulin/acacia gum complex coacervation by diffusing-wave spectroscopy and confocal scanning laser microscopy. *Colloids and Surfaces B: Biointerfaces* 20 (3), 267–280.
- Shah, B., Davidson, P.M., Zhong, Q., 2012a. Encapsulation of eugenol using Maillard-type conjugates to form transparent and heat stable nanoscale dispersions. *LWT* 49 (1), 139–148. <https://doi.org/10.1016/j.lwt.2012.04.029>.
- Shah, B., Ikeda, S., Michael Davidson, P., Zhong, Q., 2012b. Nanodispersing thymol in whey protein isolate-maltodextrin conjugate capsules produced using the emulsion–evaporation technique. *Journal of Food Engineering* 113 (1), 79–86. <https://doi.org/10.1016/j.jfoodeng.2012.05.019>.
- Shi, Y., Liang, R., Chen, L., et al., 2019. The antioxidant mechanism of Maillard reaction products in oil-in-water emulsion system. *Food Hydrocolloids* 87, 582–592. <https://doi.org/10.1016/j.foodhyd.2018.08.039>.
- Sinha, V.R., Kumria, R., 2001. Polysaccharides in colon-specific drug delivery. *International Journal of Pharmaceutics* 224 (1–2), 19–38.
- Sripabrom, J., Luangpituksa, P., Wongkongkatep, J., Pongtharangkul, T., Suphantharika, M., 2019. Influence of pH and ionic strength on the physical and rheological properties and stability of whey protein stabilized o/w emulsions containing xanthan gum. *Journal of Food Engineering* 242, 141–152. <https://doi.org/10.1016/j.jfoodeng.2018.08.031>.
- Timilsena, Y.P., Adhikari, B., Barrow, C.J., 2017. Digestion behaviour of chia seed oil encapsulated in chia seed protein-gum complex coacervates. *Food Hydrocolloids* 66, 71–81. <https://doi.org/10.1016/j.foodhyd.2016.12.017>.
- Tromp, R.H., van de Velde, F., van Riel, J., Paques, M., 2001. Confocal scanning light microscopy (CSLM) on mixtures of gelatine and polysaccharides. *Food Research International* 34 (10), 931–938.
- Tu, Y., Xu, Y., Ren, F., Zhang, H., 2020. Characteristics and antioxidant activity of Maillard reaction products from α -lactalbumin and 2'-fucosyllactose. *Food Chemistry* 316, 126341. <https://doi.org/10.1016/j.foodchem.2020.126341>.
- Vaclavik, V.A., Christian, E.W., 2008. Proteins in food: An introduction. In: Vaclavik, V.A., Christian, E.W. (Eds.), *Essentials of Food Science*. Springer, pp. 145–159. https://doi.org/10.1007/978-0-387-69940-0_8.
- Wang, B., Adhikari, B., Barrow, C.J., 2014. Optimisation of the microencapsulation of tuna oil in gelatin–sodium hexametaphosphate using complex coacervation. *Food Chemistry* 158, 358–365.
- Wang, C., Liu, Z., Xu, G., Yin, B., Yao, P., 2016. BSA-dextran emulsion for protection and oral delivery of curcumin. *Food Hydrocolloids* 61, 11–19.
- Weinbreck, F., Minor, M., Kruij, C.G. de, 2004a. Microencapsulation of oils using whey protein/gum Arabic coacervates. *Journal of Microencapsulation* 21 (6), 667–679. <https://doi.org/10.1080/02652040400008499>.
- Weinbreck, F., Rollem, H.S., Tromp, R.H., de Kruij, C.G., 2004b. Diffusivity of whey protein and gum Arabic in their coacervates. *Langmuir* 20 (15), 6389–6395.
- Weinbreck, F., Tromp, R.H., De Kruij, C.G., 2004c. Composition and structure of whey protein/gum arabic coacervates. *Biomacromolecules* 5 (4), 1437–1445.
- Weiss, J., Salminen, H., Moll, P., Schmitt, C., 2019. Use of molecular interactions and mesoscopic scale transitions to modulate protein-polysaccharide structures. *Advances in Colloid and Interface Science* 271.101987. <https://doi.org/10.1016/j.cis.2019.07.008>.
- Wijaya, W., Patel, A.R., Setiowati, A.D., Van der Meeren, P., 2017. Functional colloids from proteins and polysaccharides for food applications. *Trends in Food Science & Technology* 68, 56–69.
- Xiao, Z., Hou, W., Kang, Y., Niu, Y., Kou, X., 2019. Encapsulation and sustained release properties of watermelon flavor and its characteristic aroma compounds from γ -cyclodextrin inclusion complexes. *Food Hydrocolloids* 97.105202. <https://doi.org/10.1016/j.foodhyd.2019.105202>.

- Xie, H., Xiang, C., Li, Y., *et al.*, 2019. Fabrication of ovalbumin/ κ -carrageenan complex nanoparticles as a novel carrier for curcumin delivery. *Food Hydrocolloids* 89, 111–121. <https://doi.org/10.1016/j.foodhyd.2018.10.027>.
- Xu, D., Yuan, F., Gao, Y., *et al.*, 2014. Influence of whey protein–beet pectin conjugate on the properties and digestibility of β -carotene emulsion during in vitro digestion. *Food Chemistry* 156, 374–379. <https://doi.org/10.1016/j.foodchem.2014.02.019>.
- Xu, D., Yuan, F., Gao, Y., McClements, D.J., Decker, E.A., 2013. Influence of pH, metal chelator, free radical scavenger and interfacial characteristics on the oxidative stability of β -carotene in conjugated whey protein–pectin stabilised emulsion. *Food Chemistry* 139 (1), 1098–1104. <https://doi.org/10.1016/j.foodchem.2013.02.027>.
- Yang, Y., Cui, S.W., Gong, J., *et al.*, 2015a. A soy protein-polysaccharides Maillard reaction product enhanced the physical stability of oil-in-water emulsions containing citral. *Food Hydrocolloids* 48, 155–164. <https://doi.org/10.1016/j.foodhyd.2015.02.004>.
- Yang, Y., Cui, S., Gong, J., *et al.*, 2015b. Stability of citral in oil-in-water emulsions protected by a soy protein–polysaccharide Maillard reaction product. *Food Research International* 69, 357–363. <https://doi.org/10.1016/j.foodres.2015.01.006>.
- Yeo, Y., Bellas, E., Firestone, W., Langer, R., Kohane, D.S., 2005a. Complex coacervates for thermally sensitive controlled release of flavor compounds. *Journal of Agricultural and Food Chemistry* 53 (19), 7518–7525. <https://doi.org/10.1021/jf0507947>.
- Yeo, Y., Bellas, E., Firestone, W., Langer, R., Kohane, D.S., 2005b. Complex coacervates for thermally sensitive controlled release of flavor compounds. *Journal of Agricultural and Food Chemistry* 53 (19), 7518–7525. <https://doi.org/10.1021/jf0507947>.
- Yi, J., Lam, T.I., Yokoyama, W., Cheng, L.W., Zhong, F., 2014. Controlled release of β -carotene in β -Lactoglobulin–dextran-conjugated nanoparticles' in vitro digestion and transport with caco-2 monolayers. *Journal of Agricultural and Food Chemistry* 62 (35), 8900–8907. <https://doi.org/10.1021/jf502639k>.
- Yuan, Y., Kong, Z.-Y., Sun, Y.-E., Zeng, Q.-Z., Yang, X.-Q., 2017. Complex coacervation of soy protein with chitosan: Constructing antioxidant microcapsule for algal oil delivery. *LWT* 75, 171–179. <https://doi.org/10.1016/j.lwt.2016.08.045>.
- Zeeb, B., Yavuz-Düzgün, M., Dreher, J., *et al.*, 2018. Modulation of the bitterness of pea and potato proteins by a complex coacervation method. *Food & Function* 9 (4), 2261–2269. <https://doi.org/10.1039/C7FO01849E>.
- Zhang, X., Li, X., Liu, L., *et al.*, 2020. Covalent conjugation of whey protein isolate hydrolysates and galactose through Maillard reaction to improve the functional properties and antioxidant activity. *International Dairy Journal* 102, 104584.
- Zhang, Z.-Q., Pan, C.-H., Chung, D., 2011. Tannic acid cross-linked gelatin–gum Arabic coacervate microspheres for sustained release of allyl isothiocyanate: Characterization and in vitro release study. *Food Research International* 44 (4), 1000–1007. <https://doi.org/10.1016/j.foodres.2011.02.044>.
- Zhou, H., Sun, X., Zhang, L., *et al.*, 2012. Fabrication of biopolymeric complex coacervation core micelles for efficient tea polyphenol delivery via a green process. *Langmuir* 28 (41), 14553–14561. <https://doi.org/10.1021/la303062j>.

Further Reading

- Sanchez, C., Mekhloufi, G., Renard, D., 2006. Complex coacervation between β -lactoglobulin and Acacia gum: A nucleation and growth mechanism. *Journal of Colloid and Interface Science* 299 (2), 867–873. <https://doi.org/10.1016/j.jcis.2006.02.031>.
- Sanchez, C., Mekhloufi, G., Schmitt, C., *et al.*, 2002. Self-assembly of β -Lactoglobulin and acacia gum in aqueous solvent: Structure and phase-ordering kinetics. *Langmuir* 18 (26), 10323–10333. <https://doi.org/10.1021/la0262405>.

Polymer Matrix Composites Containing Carbon Nanomaterials for Medical Applications

Maryam Ahmadzadeh Tofighy, Soha Habibi, and Toraj Mohammadi, Iran University of Science and Technology, Tehran, Iran

© 2021 Elsevier Inc. All rights reserved.

Introduction

Today, cancer is a serious threat to human health and one of the leading causes of death worldwide. The most common cancers are lung cancer, breast cancer, colon cancer and prostate cancer. The lack of appropriate treatment is the main reason for the high rate of cancer mortality. The treatments currently used to cure cancer including chemotherapy and radiation therapy are generally costly, ineffective, and cause painful side effects. On the other hands, removing cancer cells surgically is difficult, time consuming and painful. Hence, scientists are looking for cost-effective, efficient and targeted methods for diagnosing and treating cancer (Fu *et al.*, 2016; Wilson *et al.*, 2012; Fonseca *et al.*, 2015).

Drug is a natural or artificial product that is designed to cure or prevent certain diseases. Drugs are first prescribed and their therapeutic effects are shown after dispersal in the body and reaching the desired tissue or organ. Of course, the drug treatment process can also face challenges including negative effect of the drug on healthy tissues of the body, excretion of the drug by the body before affecting the damaged tissue and metabolism or destruction of the drug before reaching the damaged tissue. The best way to solve these problems is to prescribe a drug in very high doses so that at least a small amount of the drug reaches the desired tissue. But this method is not suitable at all. Because overexposure to the drug can cause irreversible side effects on other tissues. As a result, the scientific community is looking to develop tools for effective drug delivery (Morrow *et al.*, 2007; Vasir and Labhasetwar, 2005).

In recent years, many studies have been reported on the design, synthesis, and characterization of new substances as drug delivery systems to improve drug efficacy. With the help of these new systems, the safety of treatment increases and the correct amount of drug reaches the most appropriate place in the body at the correct rate. Using these systems can prolong drug activity and reduce drug side effects. Improving the performance of these systems requires the design of new materials as drug carriers. The carriers can release active drug compounds directly into cells and distinguish cancerous tissue from healthy tissue. This method can significantly improve the therapeutic efficacy of drugs. Because with this method, drugs accumulate only in the damaged tissue and the dose control and the release rate of drug can be adjusted. The release of targeted drug is able to achieve the desired curing effect with the least amount of drug (Yang *et al.*, 2011; Daum *et al.*, 2012; Alley *et al.*, 2010).

Today, nanotechnology has revolutionized the treatment of cancer by improving current cancer treatment methods as well as making new carriers and drugs. In other words, nanotechnology seeks to find an effective way to deliver drug molecules to target cancer cells without affecting healthy cells. It was found that using nanocarriers can be very effective to deliver drug molecules in a targeted manner without damaging healthy cells (Eliaz *et al.*, 2004; Shanmuganathan *et al.*, 2019; Kumari *et al.*, 2016).

Carbon nanotubes (CNTs) with unique physicochemical properties have received considerable attention particularly as effective drug nanocarriers, diagnostic tools and therapeutic agents (Guo *et al.*, 2017; Bianco *et al.*, 2005). Nowadays, composite materials based on polymeric hydrogels and CNTs (CNTs-based hydrogels) have received considerable attention of scientific community as innovative drug delivery systems. CNTs-based hydrogels with combining properties of both CNTs and hydrogels can be considered as drug delivery systems with improved mechanical, physicochemical, and biological properties (Prakash *et al.*, 2011).

Drug Delivery Fundamentals

The original idea of targeted drug delivery was first stated nearly a hundred years ago by Paul Ehrlich (Strebhardt and Ullrich (2008)). Cancer treatment is one of the most important and vital applications of targeted drug delivery. Conventional chemotherapy agents not only specifically affect cancer cells, but also affect healthy cells and have a destructive effect on them and cause harmful side effects. Therefore, modern drug delivery systems have been considered to overcome these problems. In these systems, the time, place, and rate of drug releasing are well controlled. Therefore, in addition to increase the therapeutic efficacy of the drugs, their side effects are significantly reduced. Also, anti-inflammatory drugs have many side effects, including osteoporosis, which can be reduced by targeted drug delivery (Souto *et al.*, 2010; Barkin, 2015). Each drug delivery system should have the following two characteristics:

- (1) Increasing the effectiveness of the anti-cancer drugs in cancer tissues.
- (2) Reducing the toxicity of the anti-cancer drugs in other healthy tissues.

In general, targeted drug delivery mechanisms are divided into three categories (Torchilin, 2000): physical targeting, active targeting and inactive targeting. In physical targeting, accumulation or dispersion of the drug agents in the desired tissue is done by various external forces such as magnetic field, ultrasound, light, heat and electric field. The magnetic field has been more widely

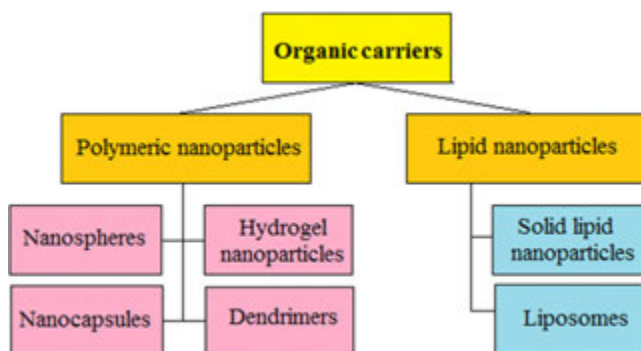


Fig. 1 Classifications of organic carriers.

used due to its cost effectiveness and ease of operation. Magnetic nanoparticles with unique properties have become attractive drug carriers for targeted drug delivery. Creating bipolar interactions under the influence of an external magnetic field leads to accumulation of the magnetic drug carriers in the target tissue (Xuan *et al.*, 2018; Lu *et al.*, 2012).

Inactive targeting is used when the target tissue has specific physiological characteristics compared to other healthy tissues which can lead to the selective accumulation of the drug in the target tissue. Drug carriers are able to use the structural features of tumor tissue for inactive targeting as follow (Hirsjarvi *et al.*, 2011):

- (1) Enzymatic inactive targeting (conversion of inactive form of drug to active form due to the presence of a specific enzyme).
- (2) Inactive targeting due to environmental acidity difference (drug releasing due to difference in pH of target tissue with other healthy tissues)
- (3) Inactive targeting due to temperature difference (drug releasing due to difference in temperature of target tissue with other healthy tissues)

Inactive targeting can be used effectively to treat cancer tissues, because physiological characteristics of cancer tissues are very different from other healthy tissues due to their high cell division (Gindy and Prud'homme, 2009; Thomas *et al.*, 2013).

Active targeting is the most advanced targeting drug delivery approach. In this method, appropriate ligands such as antibodies are attached to the surface of carriers. The attached ligands on the carriers' surface with binding to a specific antigen on the tumor surface can direct the drug to the target tissue, accurately. A suitable antigen for active targeting should be present on the surface of all cancer cells but not in healthy cells (Salarian *et al.*, 2009; Rapoport *et al.*, 2004; Abou-Jawde *et al.*, 2003; Vogel *et al.*, 2002).

In general, the most important goals of targeted drug delivery are as follow (Kumari *et al.*, 2016):

- (1) Increasing drug concentration in the target tissue (cancer cells) through physical, inactive or active targeting.
- (2) Decreasing drug concentration in normal tissue to avoid harmful side effects.
- (3) Increasing drug stability to reduce drug degradation.
- (4) Releasing maximum drug at the target tissue.
- (5) Improving biocompatibility and biodegradability of drugs.
- (6) Improving internalization and intracellular delivery.

Designing appropriate drug carrier is very important for drug delivery applications (Kumari *et al.*, 2016) The drug carrier should be selected from materials that disappear in the body after a while or do not cause any harmful effects on the body (Vasir and Labhasetwar, 2005). Drug carriers are classified into two groups: organic and inorganic carriers. The most important inorganic carriers are ceramic nanoparticles, metal nanoparticles, magnetic nanoparticles, carbon nanomaterials such as carbon nanotubes (CNTs) and graphene oxide (GO) and etc. Among inorganic carrier, CNTs with unique physical and chemical properties have received considerable attention for drug delivery applications. The classification of organic carriers is shown in Fig. 1. Among organic carrier, hydrogels with unique physical and chemical properties can be used in drug delivery applications, more effectively. Nowadays, polymer matrix composites as a combination of organic and inorganic nanomaterials have received considerable attention for drug delivery applications.

Bibliometric Analysis

The main aspects related to the medical applications of the CNTs-based polymer matrix composites materials can be identified by bibliometric analysis. The number of scholarly studies including books, book articles, journal articles, conference proceeding articles, dissertations, etc., in this research field, over time is illustrated in Fig. 2. As observed, the number of scholarly studies accomplished over the years of 1999–2015 have been significantly increased and then over the years of 2015–2021 decreased. The journal articles have the highest share 89.2%. Fig. 3 shows the top publishers by the number of scholarly works in this field. As can



Fig. 2 Scholarly studies in the field of medical applications of the CNTs-based polymer matrix composites over time. Reprinted from lens.org.

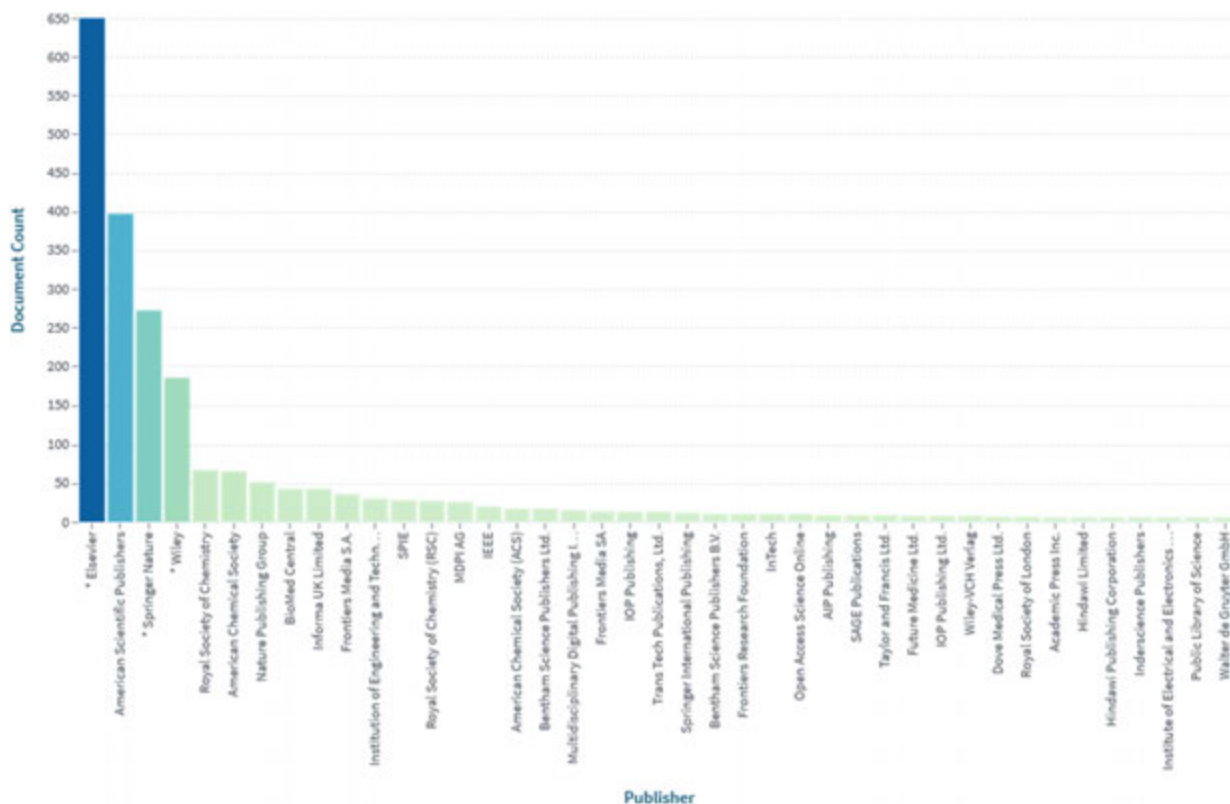


Fig. 3 The top publishers based on the number of accomplished scholarly studies in the field of medical applications of the CNTs-based polymer matrix composites. Reprinted from lens.org.

be observed, Elsevier, American Scientific, Springer nature and Wiley publishers have been published the greatest number of the scholarly works in this research field, respectively. The activity of various countries/regions in this research field based on the number of their scholarly works is shown in Fig. 4. As can be observed, United States of America with 428 scholarly works and China with 423 scholarly works have been the most actively engaged so far. The clusters network visualization of the keywords with the most frequent co-occurrence in this research field is shown in Fig. 5. This chart was obtained by importing the data downloaded from the Scopus into the VOSviewer software (version 1.6.15) and provided valuable information about the scholarly studies conducted so far in this research field. Each circle represents a keyword. The bigger the circle, the bigger the

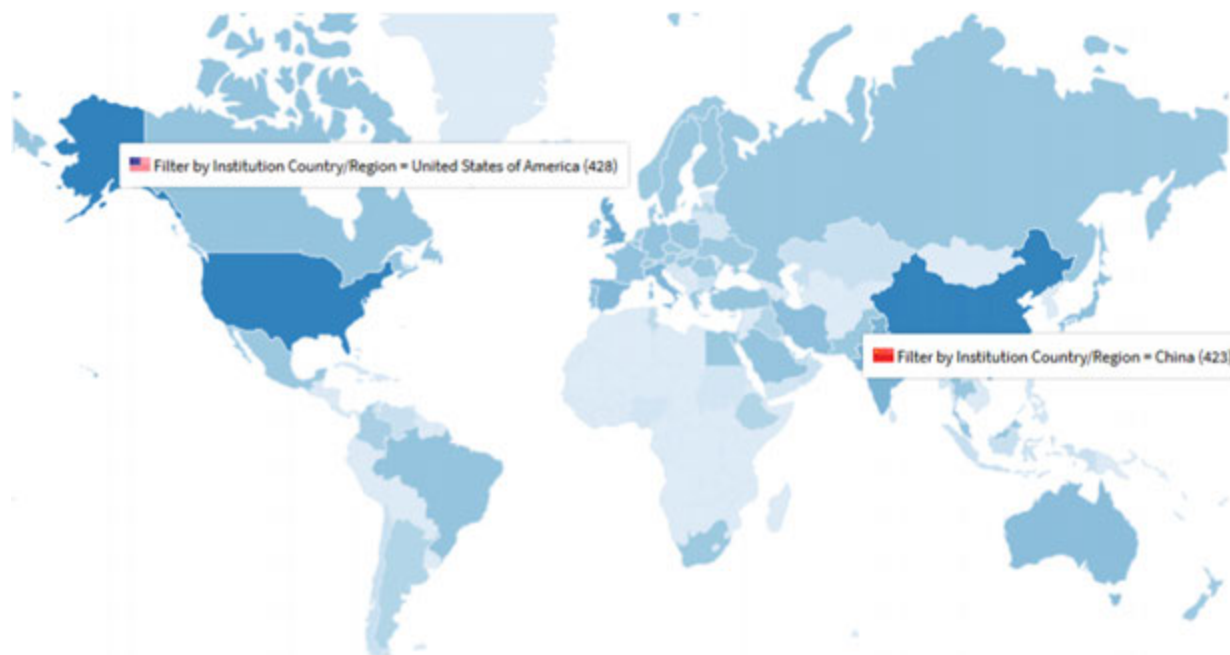


Fig. 4 The activity of various countries/regions in the field of medical applications of the CNTs-based polymer matrix composites based on the number of scholarly works. Reprinted from lens.org.

occurrence. The co-occurrence relationship between the keywords is presented by curves. Moreover, the distance between two keywords indicates the relationship strength, i.e., the closer the keywords, they are the more related and vice versa. As can be observed in Fig. 5, the keywords are divided into three clusters with different colors:

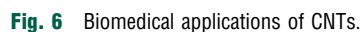
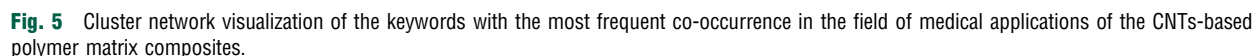
- (1) Cluster 1 (in green) mainly includes the keywords related to the topic of applications of the CNTs-based polymer matrix composites in drug delivery, such as “drug delivery systems”, “targeted drug delivery”, “metabolism”, “cytotoxicity”, “DNA”, “body fluids”, “biomaterials”, “genetic”, “human”, “nonhuman”, “animals”, “composite materials”, “multi-walled carbon nanotubes”, and “carbon nanotubes”.
- (2) Cluster 2 (in red) mainly includes the keywords related to the topic of applications of the CNTs-based polymer matrix composites in tissue engineering, such as “bone”, “tissue engineering”, “tissue”, “reinforcement”, “composites”, “composite films”, “electrospinning”, “nanofiber”, “mechanical properties”, “biological properties”, “biocompatibility”, “fillers”, “cross-linking” and “single-walled carbon nanotubes”.
- (3) Other clusters mainly include the keywords related to the CNTs-based polymer matrix composites fabrication and their properties, such as “FTIR”, “XRD”, “SEM”, “hardness”, “sintering”, “hydroxyapatite”, “titanium alloys”, “chitosan”, “hydrogels”, “corrosion resistance coating”, “mechanical properties”, “electrophoresis deposition”, “biological materials”, “polymer”, “nanoparticles”, “carbon nanotubes”, “cellulose”, “conducting polymer” and “optical properties”.

These three clusters reveal the major research directions in the field of medical applications of the CNTs-based polymer matrix composites. It is obvious that the CNTs-based polymer matrix composites can be used in drug delivery systems and tissue engineering, effectively.

Carbon Nanotubes: Properties, Functionalization and Drug Delivery Applications

In recent years, carbon nanotubes (CNTs) with unique physical and chemical properties have found many applications in various scientific fields. Recent researches have focused on the application of CNTs in biomedical applications. CNTs with high surface to volume ratio have high loading capacity of drugs and can be used effectively in fabrication of drug delivery systems. CNT based devices can be successfully utilized in stem cell based therapeutic and tissue engineering applications, including bone formation, myocardial therapy, and neuronal and muscle regeneration. Furthermore, CNTs are excellent agents for imaging and biology detection due to their distinct optical properties such as strong Raman shift, high absorption in the near-infrared (NIR) range and photoluminescence properties. CNTs with high surface area for molecular recognition molecules attachment can be used in fabrication of targeted nanodevices for selective sensing and imaging (Shao *et al.*, 2013; Ando, 2010; Simon *et al.*, 2019). Various biomedical applications of CNTs is shown in Fig. 6.

CNTs as cylindrical macromolecules are composed of a hexagonal honeycomb arrangement of carbon atoms with sp^2 hybridization. CNTs can be single-walled (SWCNTs) or multi-walled (MWCNTs) with interlayer distance between walls of 0.34



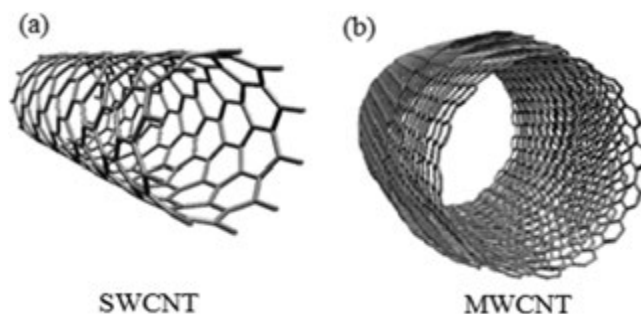


Fig. 7 Carbon nanotubes: (a) SWCNT and (b) MWCNT.

nm (graphite interlayer distance) as shown in **Fig. 7**. The outer diameter of SWCNTs and MWCNTs is in the ranges of 0.6–2.5 and 2.5–100 nm, respectively. Raw CNTs tend to form nanotube clusters due to attractive van der Waals forces between the tubes. Lack of ability to disperse in water severely limits the use of raw CNTs with hydrophobic nature in biomedical applications. On the other hands, the shelf life of the raw CNTs in biological systems has raised concerns about the use of these materials. Functionalization of CNTs is needed to overcome these limitations (Foldvari and Bagonluri, 2008; Donaldson *et al.*, 2006; Hirsch and Vostrowsky, 2005; Tofighy and Mohammadi, 2019).

CNTs with unique physicochemical properties and high surface to volume ratio and high loading capacity of drugs provide a promising drug delivery system. CNTs with high aspect ratio are more appropriate for drug delivery applications than other types of spherical nanoparticles, because, the hollow and needle-like structure of CNTs allow loading large amounts of drugs in to their hollow structure without affecting their cell penetration capability. CNTs with the adequate loading capacity can carry multi-functional therapeutics, such as drugs, genes and targeting molecules, into one cell to exert multi-valence effects (Bianco *et al.*, 2005; Shao *et al.*, 2013; Simon *et al.*, 2019).

Pharmaceutically active compounds can be loaded onto CNTs in the following three ways (Bianco *et al.*, 2005; Liu *et al.*, 2008):

- (1) Drugs can be encapsulated inside the CNT channel.
- (2) Drugs can be attached to the functional groups on the outer surface of CNTs.
- (3) Drugs can be loaded into the CNTs network as a porous adsorbent.

Hydrophilicity and biological compatibility are important preconditions for nanocarriers used in drug delivery systems. One of the obstacles to the development of CNTs as drug carriers is the hydrophobicity of the graphene side walls of the nanotubes (hydrophobic nature) as well as the strong van der Waals interactions between the nanotubes that cause the nanotubes to accumulate in aqueous solutions. To achieve successful dispersion of the CNTs, the hydrophobic surface of CNTs must be functionalized to reduce bundle formation (Bianco *et al.*, 2005; Shao *et al.*, 2013).

Four effective methods have been proposed to create uniform and stable dispersion of CNTs in aqueous medium (Hirsch and Vostrowsky, 2005; Foldvari and Bagonluri, 2008; Meng *et al.*, 2009):

- (1) Surfactant-assisted dispersion
- (2) Solvent-assisted dispersion
- (3) Biomolecules-assisted dispersion
- (4) Functionalization of the CNTs side walls with various functional groups

Among these methods, functionalization as the most effective method, with the ability to reduce toxicity, improve biocompatibility and create suitable active sites for binding to drug molecules, proteins and genes for the development of drug delivery systems has received much attention Liu *et al.* (2008). CNTs functionalization can be done in two ways: covalently or non-covalently.

Covalent Functionalization

A powerful strategy to introduce numerous functional groups on the CNTs structure is covalent functionalization. Covalent functionalization secures more stable and hydrophilic derivatives than non-covalent functionalization and remarkably facilitates the CNTs dispersion in aqueous solutions and various solvents. Covalent functionalization with altering the carbon atoms hybridization from sp^2 to sp^3 , disrupt the CNTs aromatic character. Oxidation is the most popular form of covalent functionalization which inherently generates oxygen-containing functional groups as polar groups including hydroxyl, carbonyl, carboxyl and epoxy on defect sites and both tips of CNTs which improve dispersion ability of CNTs, significantly. In the oxidation method, drastic reaction conditions, such as CNTs refluxing in strong acids such as HNO_3/H_2SO_4 , HNO_3 , $KMnO_4/H_2SO_4$ and etc. are needed. The oxidation reactions cause structural defects over the tubular structure of CNTs and therefore damage the CNTs structural integrity. Also, loss of small diameter CNTs and even loss of the entire material as well as shortening of the tubes length, are another drawbacks of the oxidation method. Carboxylic acids groups permit further incorporation of other functional groups

on the CNTs structure. However, at first, pre-activation of these functional groups either by coupling agents such as carbodiimides and hydroxybenzotriazole or by acyl chlorides such as thionyl chloride or oxalyl chloride is necessary (Shao *et al.*, 2013; Meng *et al.*, 2009; Tofghy and Mohammadi, 2019; Hu *et al.*, 2003; Karousis *et al.*, 2010; Georgakilas *et al.*, 2002).

Non-Covalent Functionalization

Non-covalent functionalization methods are conventionally carried out under simple reaction conditions such as sonication and centrifuge, and obviate the necessity of harsh reactions conditions and strong reagents and appear to be more favorable than covalent functionalization methods. In addition, non-covalent functionalization methods do not damage the CNTs aromatic structure as well as the structural integrity of both graphitic tips and surface. The main drawbacks of the non-covalent functionalized CNTs are low durability of the non-covalent conjugates which may even undergo exchange with serum proteins or may dissociate from CNTs in biological fluids. This undesirable performance may cause toxicity and some other harmful outcomes undoubtedly.

Non-covalent functionalization can be performed by polymers, surfactants, and biological materials including nucleic acids, proteins, and peptides incorporation on the outer walls of CNTs by simple physical adsorption through van der Waals forces, π - π interactions and etc. As reported in the literature, it appears that the molecules containing aromatic groups (for example sodium dodecyl benzene sulfonate (SDBS) or biopolymers including peptides and single-stranded nucleic acids containing aromatic acids) can better improve dispersion ability of CNTs as a result of better π - π interactions. It should be mentioned that these materials are bonded on the outer walls of CNTs in divergent geometries for example surfactants form micelle-like assemblies around CNTs and polymeric materials wrap around CNTs to maximize van der Waals interactions (Shao *et al.*, 2013; Tofghy and Mohammadi, 2019; Kim *et al.*, 2012; Tasis *et al.*, 2003).

Polymeric Hydrogels

Polymeric hydrogels as promising bio-materials have received considerable attention. Hydrogels are composed of crosslinked hydrophilic polymer networks that are insoluble in water and can hold large amounts of biological fluids in the space between their polymer chains. The water holding capacity of hydrogels depends on the amount of hydrophilic functional groups including hydroxyl, carboxyl, amido and amino groups, etc. in the polymer chains. The hydrogels water content can be from 10% to thousands times of the dry polymer network weight. In addition, hydrogels with excellent biocompatibility can be employed in medical applications including artificial organs, tissue engineering, contact lenses, wound dressings, prostheses, and drug delivery systems (Singh and Pal, 2008; Sorbara *et al.*, 2009; Wu *et al.*, 2007).

Hydrogels can be natural or synthetic, based on their origins. The natural origins of hydrogels include chitosan and chitin, (Bobokalonov *et al.*, 2012) dextran, (Cirillo *et al.*, 2014) alginic acid, (Li *et al.*, 2012) agarose, (Zhang *et al.*, 2012) pectin, (Della Rocca *et al.*, 2012) and different derivatives of these polymers and the synthetic origins of hydrogels are included polyvinyl alcohol (PVA), (Zhang *et al.*, 2012) polyethylene glycol (PEG), (Kost and Langer, 2012) polyacrylamide (PAM), (Zhu *et al.*, 2012) polyacrylic acid (PAA) (He *et al.*, 2008) and polymethyl methacrylate (PMA) (Samanta *et al.*, 2012).

Hydrogels are classified into permanent and non-permanent hydrogels based on the nature of their crosslinking. In permanent (chemical) hydrogels, covalent bonds are formed between the polymer chains during the crosslinking reaction (for example hydrogels based on acrylic monomers). In non-permanent (physical) hydrogels, the polymer chains are crosslinked by formation of physical interactions including ionic, van der Waals and hydrogen interactions and molecular entanglement (for example agar-agar and gelatin hydrogels) (Cirillo *et al.*, 2014; Hoffman, 2012).

Some hydrogels that are able to respond to external stimuli by changing phase or changing equilibrium are referred to as "smart" or "stimuli-responsive" hydrogels. Smart hydrogels have been used in targeted drug delivery due to their ability to respond to the environmental parameters such as biochemical, chemical and physical stimuli. The most important physical stimuli are pressure, temperature, sound, light, and magnetic and electric fields, while chemical stimuli include pH, ions, ionic strength and so on (Kim *et al.*, 2003; Li *et al.*, 2004).

Basis on the external stimuli type, smart hydrogels are divided into heat-sensitive hydrogels, pH-sensitive hydrogels, light-sensitive hydrogels, electro-sensitive hydrogels and so on. External stimuli can be applied to hydrogels in a variety of ways, such as the use of potassium phosphate buffer for pH-sensitive hydrogels, the use of IR irradiation and/or hot plates for heat-sensitive hydrogels, the use of voltage by appropriate inert electrodes for electro-sensitive hydrogels and so on (Yun *et al.*, 2010).

Hydrogels with high water content and soft and elastomeric nature resemble living tissues which minimizing frictional and mechanical irritation. Hydrogels with low interfacial tension exhibit minimal tendency to proteins absorption from body fluids and cell adhesion. Furthermore, the swelling capacity of hydrogels causes the removal of reagent residues to be easy. The biggest disadvantage of hydrogels is their high water content which causes their poor mechanical properties. The mechanical properties of hydrogels can be improved through chemical crosslinking (preparation of interpenetrating polymer networks (IPN)). However, the disadvantage of chemical crosslinking method is the presence of residual crosslinking agents resulting in some toxic side effects. Other limitations of hydrogels using as drug delivery systems are burst or incomplete therapeutic agent release as well as poor scalability of their manufacturing processes (Cirillo *et al.*, 2011; Altimari *et al.*, 2012; Li *et al.*, 2003). In order to overcome

these drawbacks, hydrogel composites materials as a combination of nanomaterials and polymeric chains have been recently developed.

Hydrogel Composites

To enhance drug release profile, mechanical strength, biological interactions and remote actuation capabilities of hydrogels, hydrogel composites have been developed by incorporation of nanomaterials into hydrogel matrices for biomedical and pharmaceutical applications. Hydrogel composites containing different nanomaterials, including gold, clay, silver, CNTs, iron oxide, tricalcium phosphate and hydroxyapatite as fillers have been developed as biomaterials (Satarkar *et al.*, 2010; Lovinger, 2005). Among these composites, CNTs-based hydrogel composites with unique physicochemical properties have received considerable attention for drug delivery applications.

CNTs-based hydrogel composites

The first CNTs-based polymer nanocomposite was reported in 1994 by DeHeer *et al.* (1995). Nowadays, CNTs have been recognized as appropriate nanofiller to improve the physicochemical properties of polymers. As reported in the literature, the CNTs-based hydrogel composites can be used effectively in many fields including semiconductor device manufacturing, nanobiotechnology, molecular recognition, nanofluidics, catalysis, drug delivery and molecule specific chemobiosensing. Therefore, finding new effective methods to fabricate the CNTs-based hydrogels have received considerable attention. As reported in the literature, the covalent and non-covalent functionalization of CNTs with polymeric materials are the main adopted synthesis approach of the CNTs-based hydrogel composites. As mentioned in the previous section, in the non-covalent functionalization method, the intrinsic properties of CNTs don't change, however, in the covalent functionalization method, with changing hybridization of carbon atoms from sp^2 to sp^3 , abundant functional groups are formed on the CNTs sidewall structure. In the covalent functionalization, the CNTs sidewalls with sp^2 hybridization contain highly delocalized π electrons which bond with π electron rich compounds through π - π interactions. This organic functionalization method avoids changing the CNTs intrinsic structures and the structurally intact functionalized CNTs are fabricated (Wang *et al.*, 2004). The CNTs-based polymeric composites fabrication through the covalent functionalization method consists of "grafting from" and "grafting to" methods (Liu *et al.*, 2004; Baskaran *et al.*, 2004). In the "grafting from" method, monomers are polymerized on the surface of CNTs from surface-derived initiators, while the "grafting to" method involves the polymeric chains reaction with the either raw or pre-functionalized CNTs. Low grafting density is the main limitation of the "grafting to" technique due to initial binding of polymer chains sterically that hinders diffusion of additional macromolecules to the surface of CNTs. The "grafting from" approach causes to obtain efficiently grafted polymers with high molecular weight on the CNTs surface, because polymer growth is not limited by the steric hindrance. Therefore, functionalized CNTs with high polymer grafting density can be fabricated through the "grafting from" approach (Yan and Yang, 2009; Mylvaganam and Zhang, 2004). Many techniques including "click" chemistry, (Li *et al.*, 2005) esterification, (Gao *et al.*, 2007) pyrene moiety adsorption, (Martin *et al.*, 2004) layer-by-layer self-assembly, (Kong *et al.*, 2005) radical coupling, (Cirillo *et al.*, 2013) anionic coupling, (Huang *et al.*, 2004) supercritical CO_2 -solubilized polymerization or coating, (Dai *et al.*, 2004) radical polymerization, (Qin *et al.*, 2004) γ -ray irradiation, (Xu *et al.*, 2006) polycondensation, (Zeng *et al.*, 2006) cathodic electrochemical grafting, (Petrov *et al.*, 2004) reversible addition fragmentation chain-transfer (RAFT) polymerization, (Xu *et al.*, 2006) ring-opening polymerization (Qu *et al.*, 2005) and anionic polymerization (Chen *et al.*, 2006) have been used for fabrication of the CNTs-based polymeric composites.

Conclusions

Cancer is one of the leading causes of death worldwide. Today, nanotechnology has revolutionized the cancer treatment by improving current cancer treatment methods as well as making new drug and drug carriers. CNTs as a one-dimensional nanomaterial with unique physicochemical properties including high drug-loading, excellent penetrating capability in the cellular barriers, easy modification with other molecules, large surface area, excellent electronic, magnetic and thermal properties, and good pH-dependent unloading capacity can be employed as an efficient and promising delivery system of many therapeutic active compounds, ranging from cardiovascular drugs, antineoplastic agents, anti-inflammatory, anti-infective and anti-cancer drugs, and genes. Polymeric hydrogels as promising bio-materials have also received considerable attention for drug delivery applications. But the main limitations of the hydrogels as drug delivery systems are burst or incomplete therapeutic agent release as well as poor scalability of their manufacturing processes. In order to overcome these drawbacks, hydrogel composites materials as a combination of nanomaterials and polymeric chains have been recently developed. CNTs-based hydrogels with improved mechanical, physicochemical, and biological properties than hydrogels can be considered as appropriate drug delivery systems.

References

- Abou-Jawde, R., Choueiri, T., Alemany, C., Mekhail, T., 2003. An overview of targeted treatments in cancer. *Clinical Therapeutics* 25, 2121–2137.
 Alley, S.C., Okeley, N.M., Senter, P.D., 2010. Antibody–drug conjugates: Targeted drug delivery for cancer. *Current Opinion in Chemical Biology* 14, 529–537.

- Altamari, I., Spizzirri, U., Iemma, F., *et al.*, 2012. pH-sensitive drug delivery systems by radical polymerization of gelatin derivatives. *Journal of Applied Polymer Science* 125, 3006–3013.
- Ando, Y., 2010. Carbon nanotube: The inside story. *Journal of Nanoscience and Nanotechnology* 10, 3726–3738.
- Barkin, R.L., 2015. Topical nonsteroidal anti-inflammatory drugs: The importance of drug, delivery, and therapeutic outcome. *American Journal of Therapeutics* 22, 388–407.
- Baskaran, D., Mays, J.W., Bratcher, M.S., 2004. Polymer-grafted multiwalled carbon nanotubes through surface-initiated polymerization. *Angewandte Chemie* 116, 2190–2194.
- Bianco, A., Kostarelos, K., Prato, M., 2005. Applications of carbon nanotubes in drug delivery. *Current Opinion in Chemical Biology* 9, 674–679.
- Bobokolonov, D., Mukhidinov, Z., Rakhimov, I., *et al.*, 2012. Piroxicam ex vivo release kinetics from zein/pectin delivery systems. *Pharmaceutical Chemistry Journal* 46, 378–380.
- Chen, S., Chen, D., Wu, G., 2006. Grafting of poly (tBA) and PtBA-b-PMMA onto the surface of SWNTs using carbanions as the initiator. *Macromolecular Rapid Communications* 27, 882–887.
- Cirillo, G., Iemma, F., Spizzirri, U.G., *et al.*, 2011. Synthesis of stimuli-responsive microgels for in vitro release of diclofenac diethyl ammonium. *Journal of Biomaterials Science* 22, 823–844.
- Cirillo, G., Caruso, T., Hampel, S., *et al.*, 2013. Novel carbon nanotube composites by grafting reaction with water-compatible redox initiator system. *Colloid and Polymer Science* 291, 699–708.
- Cirillo, G., Hampel, S., Spizzirri, U.G., *et al.*, 2014. Carbon nanotubes hybrid hydrogels in drug delivery: A perspective review. *BioMed Research International* 2014.
- Dai, X., Liu, Z., Han, B., *et al.*, 2004. Carbon nanotube/poly (2, 4-hexadiyne-1, 6-diol) nanocomposites prepared with the aid of supercritical CO₂. *Chemical Communications* 2190–2191.
- Daum, N., Tscheka, C., Neumeyer, A., Schneider, M., 2012. Novel approaches for drug delivery systems in nanomedicine: Effects of particle design and shape. *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology* 4, 52–65.
- DeHeer, W.A., Bacsá, W., Chatelain, A., *et al.*, 1995. Aligned carbon nanotube films: Production and optical and electronic properties. *Science* 268, 845–847.
- Della Rocca, D.G., Willenberg, B.J., Ferreira, L.F., *et al.*, 2012. A degradable, bioactive, gelatinized alginate hydrogel to improve stem cell/growth factor delivery and facilitate healing after myocardial infarction. *Medical Hypotheses* 79, 673–677.
- Donaldson, K., Aitken, R., Tran, L., *et al.*, 2006. Carbon nanotubes: A review of their properties in relation to pulmonary toxicology and workplace safety. *Toxicological Sciences* 92, 5–22.
- Eliaz, R.E., Nir, S., Marty, C., Szoka, F.C., 2004. Determination and modeling of kinetics of cancer cell killing by doxorubicin and doxorubicin encapsulated in targeted liposomes. *Cancer Research* 64, 711–718.
- Foldvari, M., Bagonluri, M., 2008. Carbon nanotubes as functional excipients for nanomedicines: I. Pharmaceutical properties. *Nanomedicine: Nanotechnology, Biology and Medicine* 4, 173–182.
- Foldvari, M., Bagonluri, M., 2008. Carbon nanotubes as functional excipients for nanomedicines: ii. Drug delivery and biocompatibility issues. *Nanomedicine: Nanotechnology, Biology and Medicine* 4, 183–200.
- Fonseca, A.C., Serra, A.C., Coelho, J.F., 2015. Bioabsorbable polymers in cancer therapy: Latest developments. *EPMA Journal* 6.22.
- Fu, S., Xia, J., Wu, J., 2016. Functional chitosan nanoparticles in cancer treatment. *Journal of Biomedical Nanotechnology* 12, 1585–1603.
- Gao, C., Muthukrishnan, S., Li, W., *et al.*, 2007. Linear and hyperbranched glycopolymer-functionalized carbon nanotubes: Synthesis, kinetics, and characterization. *Macromolecules* 40, 1803–1815.
- Georgakilas, V., Tagmatarchis, N., Pantarotto, D., *et al.*, 2002. Amino acid functionalisation of water soluble carbon nanotubes. *Chemical Communications* 3050–3051.
- Gindy, M.E., Prud'homme, R.K., 2009. Multifunctional nanoparticles for imaging, delivery and targeting in cancer therapy. *Expert Opinion on Drug Delivery* 6, 865–878.
- Guo, Q., Shen, X.-T., Li, Y.-y., Xu, S.-q., 2017. Carbon nanotubes-based drug delivery to cancer and brain. *Current Medical Science* 37, 635–641.
- He, H., Li, L., Lee, L.J., 2008. Photopolymerization and structure formation of methacrylic acid based hydrogels: The effect of light intensity. *Reactive and Functional Polymers* 68, 103–113.
- Hirsch, A., Vostrowsky, O., 2005. Functionalization of carbon nanotubes. *Functional Molecular Nanostructures* 193–237.
- Hirsjarvi, S., Passirani, C., Benoit, J.-P., 2011. Passive and active tumour targeting with nanocarriers. *Current Drug Discovery Technologies* 8, 188–196.
- Hoffman, A.S., 2012. Hydrogels for biomedical applications. *Advanced Drug Delivery Reviews* 64, 18–23.
- Hu, H., Zhao, B., Itkis, M.E., Haddon, R.C., 2003. Nitric acid purification of single-walled carbon nanotubes. *The Journal of Physical Chemistry B* 107, 13838–13842.
- Huang, H.M., Liu, I.C., Chang, C.Y., *et al.*, 2004. Preparing a polystyrene-functionalized multiple-walled carbon nanotubes via covalently linking acyl chloride functionalities with living polystyryllithium. *Journal of Polymer Science Part A: Polymer Chemistry* 42, 5802–5810.
- Karousis, N., Tagmatarchis, N., Tasis, D., 2010. Current progress on the chemical modification of carbon nanotubes. *Chemical Reviews* 110, 5366–5397.
- Kim, S.J., Yoon, S.G., Lee, Y.M., Kim, S.I., 2003. Electrical sensitive behavior of poly (vinyl alcohol)/poly (diallyldimethylammonium chloride) IPN hydrogel. *Sensors and Actuators B: Chemical* 88, 286–291.
- Kim, S.W., Kim, T., Kim, Y.S., *et al.*, 2012. Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon* 50, 3–33.
- Kong, H., Luo, P., Gao, C., Yan, D., 2005. Polyelectrolyte-functionalized multiwalled carbon nanotubes: Preparation, characterization and layer-by-layer self-assembly. *Polymer* 46, 2472–2485.
- Kost, J., Langer, R., 2012. Responsive polymeric delivery systems. *Advanced Drug Delivery Reviews* 64, 327–341.
- Kumari, P., Ghosh, B., Biswas, S., 2016. Nanocarriers for cancer-targeted drug delivery. *Journal of Drug Targeting* 24, 179–191.
- Li, H., Yuan, Z., Lam, K., *et al.*, 2004. Model development and numerical simulation of electric-stimulus-responsive hydrogels subject to an externally applied electric field. *Biosensors and Bioelectronics* 19, 1097–1107.
- Li, H., Cheng, F., Duft, A.M., Adronov, A., 2005. Functionalization of single-walled carbon nanotubes with well-defined polystyrene by “click” coupling. *Journal of the American Chemical Society* 127, 14518–14524.
- Li, H., Wang, D.Q., Chen, H.L., Liu, B.L., Gao, L.Z., 2003. A novel gelatin–carbon nanotubes hybrid hydrogel. *Macromolecular Bioscience* 3, 720–724.
- Li, P., Dou, X.-Q., Tang, Y.-T., *et al.*, 2012. Gelator-polysaccharide hybrid hydrogel for selective and controllable dye release. *Journal of Colloid and Interface Science* 387, 115–122.
- Liu, I.-C., Huang, H.-M., Chang, C.-Y., *et al.*, 2004. Preparing a styrenic polymer composite containing well-dispersed carbon nanotubes: anionic polymerization of a nanotube-bound p-methylstyrene. *Macromolecules* 37, 283–287.
- Liu, Z., Chen, K., Davis, C., *et al.*, 2008. Drug delivery with carbon nanotubes for in vivo cancer treatment. *Cancer Research* 68, 6652–6660.
- Loving, A.J., 2005. Nano-, Bio-, Multi-, Inter-,...: polymer Research in an Era of Prefixes. *Journal of Macromolecular Science Part C: Polymer Reviews* 45, 195–199.
- Lu, Y.-J., Wei, K.-C., Ma, C.-C.M., Yang, S.-Y., Chen, J.-P., 2012. Dual targeted delivery of doxorubicin to cancer cells using folate-conjugated magnetic multi-walled carbon nanotubes. *Colloids and Surfaces B: Biointerfaces* 89, 1–9.
- Martin, R.B., Qu, L., Lin, Y., *et al.*, 2004. Functionalized carbon nanotubes with tethered pyrenes: Synthesis and photophysical properties. *The Journal of Physical Chemistry B* 108, 11447–11453.
- Meng, L., Fu, C., Lu, Q., 2009. Advanced technology for functionalization of carbon nanotubes. *Progress in Natural Science* 19, 801–810.
- Morrow Jr, K.J., Bawa, R., Wei, C., 2007. Recent advances in basic and clinical nanomedicine. *Medical Clinics of North America* 91, 805–843.
- Mylvaganam, K., Zhang, L., 2004. Nanotube functionalization and polymer grafting: An ab initio study. *The Journal of Physical Chemistry B* 108, 15009–15012.
- Petrov, P., Lou, X., Pagnoulle, C., *et al.*, 2004. Functionalization of multi-walled carbon nanotubes by electrografting of polyacrylonitrile. *Macromolecular rapid communications* 25, 987–990.

- Prakash, S., Malhotra, M., Shao, W., Tomaro-Duchesneau, C., Abbasi, S., 2011. Polymeric nanohybrids and functionalized carbon nanotubes as drug delivery carriers for cancer therapy. *Advanced Drug Delivery Reviews* 63, 1340–1351.
- Qin, S., Qin, D., Ford, W.T., Herrera, J.E., Resasco, D.E., 2004. Grafting of poly (4-vinylpyridine) to single-walled carbon nanotubes and assembly of multilayer films. *Macromolecules* 37, 9963–9967.
- Qu, L., Veca, L.M., Lin, Y., *et al.*, 2005. Soluble nylon-functionalized carbon nanotubes from anionic ring-opening polymerization from nanotube surface. *Macromolecules* 38, 10328–10331.
- Rapoport, N., Christensen, D., Fain, H., Barrows, L., Gao, Z., 2004. Ultrasound-triggered drug targeting of tumors in vitro and in vivo. *Ultrasonics* 42, 943–950.
- Salarian, M., Solati, H.M., Shafiei, S., Nemat, A., Salarian, R., 2009. Effect of hydrothermal temperature on the composition and morphology of surfactant-assisted hydrothermally synthesized hydroxyapatite nano particles. *Industrial Engineering & Management Sharif* 25 (47).
- Samanta, S., Das, S., Layek, R.K., Chatterjee, D.P., Nandi, A.K., 2012. Polythiophene-g-poly (dimethylaminoethyl methacrylate) doped methyl cellulose hydrogel behaving like a polymeric AND logic gate. *Soft Matter* 8, 6066–6072.
- Satarkar, N.S., Johnson, D., Marrs, B., *et al.*, 2010. Hydrogel-MWCNT nanocomposites: Synthesis, characterization, and heating with radiofrequency fields. *Journal of Applied Polymer Science* 117, 1813–1819.
- Shanmuganathan, R., Edison, T.N.J.I., LewisOscar, F., *et al.*, 2019. Chitosan nanopolymers: An overview of drug delivery against cancer. *International Journal of Biological Macromolecules* 130, 727–736.
- Shao, W., Arghya, P., Yiyong, M., Rodes, L., Prakash, S., 2013. Carbon nanotubes for use in medicine: Potentials and limitations. In: Suzuki, S. (Ed.), *Syntheses and Applications of Carbon Nanotubes and Their Composites*, vol. 13. IntechOpen, pp. 285–311.
- Simon, J., Flahaut, E., Golzio, M., 2019. Overview of carbon nanotubes for biomedical applications. *Materials* 12, 624.
- Singh, B., Pal, L., 2008. Development of sterulia gum based wound dressings for use in drug delivery. *European Polymer Journal* 44, 3222–3230.
- Sorbara, L., Jones, L., Williams-Lyn, D., 2009. Contact lens induced papillary conjunctivitis with silicone hydrogel lenses. *Contact Lens and Anterior Eye* 32, 93–96.
- Souto, E.B., Doktorova, S., Gonzalez-Mira, E., Egea, M.A., Garcia, M.L., 2010. Feasibility of lipid nanoparticles for ocular delivery of anti-inflammatory drugs. *Current Eye Research* 35, 537–552.
- Strebhardt, K., Ullrich, A., 2008. Paul Ehrlich's magic bullet concept: 100 years of progress. *Nature Reviews Cancer* 8, 473–480.
- Tasis, D., Tagmatarchis, N., Georgakilas, V., Prato, M., 2003. Soluble carbon nanotubes. *Chemistry—A European Journal* 9, 4000–4008.
- Thomas, R., Park, I.-K., Jeong, Y.Y., 2013. Magnetic iron oxide nanoparticles for multimodal imaging and therapy of cancer. *International Journal of Molecular Sciences* 14, 15910–15930.
- Tofighy, M.A., Mohammadi, T., 2019. Barrier, diffusion, and transport properties of rubber nanocomposites containing carbon nanofillers. In: Yarangalla, S., Mishra, R.K., Thomas, S., Kalarikkal, N., Maria, H.J. (Eds.), *Carbon-Based Nanofiller and Their Rubber Nanocomposites*. Elsevier, pp. 253–285.
- Torchilin, V.P., 2000. Drug targeting. *European Journal of Pharmaceutical Sciences* 11, S81–S91.
- Vasir, J.K., Labhasetwar, V., 2005. Targeted drug delivery in cancer therapy. *Technology in Cancer Research & Treatment* 4, 363–374.
- Vogel, C.L., Cobleigh, M.A., Tripathy, D., *et al.*, 2002. Efficacy and safety of trastuzumab as a single agent in first-line treatment of HER2-overexpressing metastatic breast cancer. *Journal of Clinical Oncology* 20, 719–726.
- Wang, C., Guo, Z.-X., Fu, S., Wu, W., Zhu, D., 2004. Polymers containing fullerene or carbon nanotube structures. *Progress in Polymer Science* 29, 1079–1141.
- Wilson, B., Ambika, T., Patel, R.D.K., Jenita, J.L., Priyadarshini, S., 2012. Nanoparticles based on albumin: Preparation, characterization and the use for 5-fluorouracil delivery. *International Journal of Biological Macromolecules* 51, 874–878.
- Wu, J., Wei, W., Wang, L.-Y., Su, Z.-G., Ma, G.-H., 2007. A thermosensitive hydrogel based on quaternized chitosan and poly (ethylene glycol) for nasal drug delivery system. *Biomaterials* 28, 2220–2232.
- Xu, G., Wu, W.-T., Wang, Y., *et al.*, 2006. Synthesis and characterization of water-soluble multiwalled carbon nanotubes grafted by a thermoresponsive polymer. *Nanotechnology* 17, 2458.
- Xu, H., Wang, X., Zhang, Y., Liu, S., 2006. Single-step in situ preparation of polymer-grafted multi-walled carbon nanotube composites under 60Co γ -ray irradiation. *Chemistry of Materials* 18, 2929–2934.
- Xuan, M., Shao, J., Zhao, J., *et al.*, 2018. Magnetic mesoporous silica nanoparticles cloaked by red blood cell membranes: Applications in cancer therapy. *Angewandte Chemie International Edition* 57, 6049–6053.
- Yan, D., Yang, G., 2009. A novel approach of in situ grafting polyamide 6 to the surface of multi-walled carbon nanotubes. *Materials Letters* 63, 298–300.
- Yang, L., Zhang, X., Ye, M., *et al.*, 2011. Aptamer-conjugated nanomaterials and their applications. *Advanced Drug Delivery Reviews* 63, 1361–1370.
- Yun, J., Im, J.S., Lee, Y.-S., *et al.*, 2010. pH and electro-responsive release behavior of MWCNT/PVA/PAAc composite microcapsules. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 368, 23–30.
- Zeng, H., Gao, C., Wang, Y., *et al.*, 2006. In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: Mechanical properties and crystallization behavior. *Polymer* 47, 113–122.
- Zhang, L., Zhao, J., Zhu, J., He, C., Wang, H., 2012. Anisotropic tough poly (vinyl alcohol) hydrogels. *Soft Matter* 8, 10439–10447.
- Zhang, L.-M., Wu, C.-X., Huang, J.-Y., *et al.*, 2012. Synthesis and characterization of a degradable composite agarose/HA hydrogel. *Carbohydrate Polymers* 88, 1445–1452.
- Zhu, A., Shi, Z., Jin, J., Li, G., Jiang, J., 2012. Synthesis and properties of polyacrylamide-based conducting gels with enhanced mechanical strength. *Journal of Macromolecular Science, Part B* 51, 2183–2190.

Biopolymer Matrix Composites for New Medical Applications

Zahra Shariatinia, Amirkabir University of Technology, Tehran, Iran

© 2021 Elsevier Inc. All rights reserved.

Introduction

Biopolymers are achieved from living organisms so that they are produced by plants and microbial organisms or synthesized using biological materials (Shariatinia 2019a,b; George *et al.*, 2020; Shuai *et al.*, 2020). They exhibit several benefits relative to the synthetic polymers especially due to their high biodegradability, biocompatibility and non-toxicity (Fazli *et al.*, 2016; Fazli and Shariatinia, 2017; Kabir *et al.*, 2020; Vinod *et al.*, 2020). Biopolymers are frequently employed in biomedical areas as clothing fabrics, packaging, food additives, water treatment materials, biosensors, cosmetics, absorbents, data storage compounds and industrial plastics (Kohsari *et al.*, 2016a,b; Mazloom-Jalali and Shariatinia, 2019; Negm *et al.*, 2020; Stanisz *et al.*, 2020). Biopolymers can be classified in three groups including polynucleotides, proteins and polysaccharides (Shariatinia and Fazli, 2015; Shariatinia and Barzegari, 2019; Shariatinia and Fasihozaman-Langroodi, 2019; Varaprasad *et al.*, 2020). Most biopolymers create non-immunogenic degradation products; thus, they are utilized in therapeutic purposes like porous three-dimensional scaffolds in tissue engineering, temporary prostheses, adhesion/fixation/suturing biomaterials, three-dimensional bio-printing, wound healing and sustained/controlled drug carriers (Park *et al.*, 2017; Shariatinia and Jalali, 2018; Shariatinia and Mohammadi-Denyani, 2018; Shariatinia and Mazloom-Jalali, 2019).

Recently, the biopolymer composites, principally those resulting from polysaccharides and proteins, have become highly attracting materials for application in medical fields (Rai *et al.*, 2015; Mazloom-Jalali *et al.*, 2020). These usage materials are extremely biocompatible, naturally and easily available, abundant, biodegradable, non-carcinogenic, non-mutagenic, non-immunogenic, non-irritating, edible, and reveal appropriate mechanical and hemo-compatibility features and capable of adsorbing/encapsulating bioactive agents (Shariatinia and Nikfar, 2013; Shariatinia *et al.*, 2015; Wsoo *et al.*, 2020). Also, they have biomimetic functions that are analogous to the native extracellular matrix, ECM, in human beings and other living organisms (Kazemi *et al.*, 2016; Shariatinia and Zahraee, 2017; Wei *et al.*, 2019). Biopolymer composite materials can be fabricated by mixing the biopolymer solution/melt with nano/micro-materials to exploit the advantageous characteristics of all constituents (Kim *et al.*, 2019; Shariatinia 2019a,b).

The mechanical features of biopolymer composites such as tensile and impact strengths can be greatly improved through adding inorganic, organic and hybrid nano/micro-materials into the polymer (Ong *et al.*, 2019). It is noteworthy that the biopolymer properties (such as chemical formula, molecular weight, processing method and morphology) in the composites can also greatly affect their mechanical characteristics (Shariatinia and Jalali, 2018; Shariatinia, 2019a,b). The physicochemical characteristics of biopolymer composites like solubility, morphology, structure, chemical functionalization/modification by appropriate substances, ECM biomimicry and tensile strength control their mechanical features and allow preparing them as diverse shapes for different applications including tubes, films, scaffolds, electrospun fibers, sponges, porous sponges, microbeads, dressing materials, sheets, membranes, hydrogels and microcapsules (Rousselle *et al.*, 2019).

Usually, biopolymer composites reveal higher levels of antibacterial activities compared to those of their related pure biopolymers and this is associated with the presence of nano/micro-materials within their matrixes (Fazli *et al.*, 2016; Fazli and Shariatinia, 2017). Accordingly, the biopolymer composites have been applied in numerous industries ranging from blends and additives within bioplastics to edible goods, personal hygiene, medical products, cancer/tumor treatment, wound healing, radiotherapy, tissue engineering, imaging and diagnosis, fabrication of implants, as well as delivery systems for drugs, nucleic acids, genes, peptides, proteins and vaccines (Ling *et al.*, 2018).

The most significant inorganic materials used in drug delivery include Au, Ag, TiO₂, ZnO, clay and SiO₂ nano-/micro-particles, zeolites, diatomites, graphene, carbon quantum dots, carbon nanotubes, hydroxyapatite and bioglass (Shariatinia *et al.*, 2011a,b, 2012; Shariatinia and Shahidi, 2014; Nikfar and Shariatinia, 2017a,b, 2019). Additionally, these materials can be introduced to the biopolymer matrixes as fillers in the forms of micro-/nano-particles, core-shell, yolk-shell and composites (Vatanparast and Shariatinia, 2018a,b; Kassem *et al.*, 2019; Vatanparast and Shariatinia, 2019a,b). A large number of biopolymers have been utilized to fabricate bio-composites such as chitosan, carboxymethyl chitosan, alginate, cellulose, carboxymethyl cellulose, hydroxyethylcellulose, starch, hyaluronic acid, gellan gum, acacia gum, guar gum, gelatin, chondroitin sulfated pectin and collagen (Khan and Mujahid, 2019; Yuan *et al.*, 2019; Vasvani *et al.*, 2020).

Medical Applications of Chitosan, Carboxymethyl Chitosan, Alginate and Hyaluronic Acid Composites

Chitosan (CS), carboxymethyl chitosan (CMCS), alginate and hyaluronic acid (HA) as well as their composites are well-known biopolymeric materials that are widely employed in various medical applications. Several examples are given in the following to indicate the most recent applications of these biologically important substances.

Micro-composites (with $0.151 \pm 0.49 \mu\text{m}$ mean size and spherical morphology) of CS and halloysite nanotubes were synthesized as mucoadhesive drug carriers (Sharif *et al.*, 2019). Micro-composites revealed adhesion onto the intestinal mucosa, the highest swelling value at acidic pH and released metoclopramide hydrochloride drug in a sustained manner (66.8% at

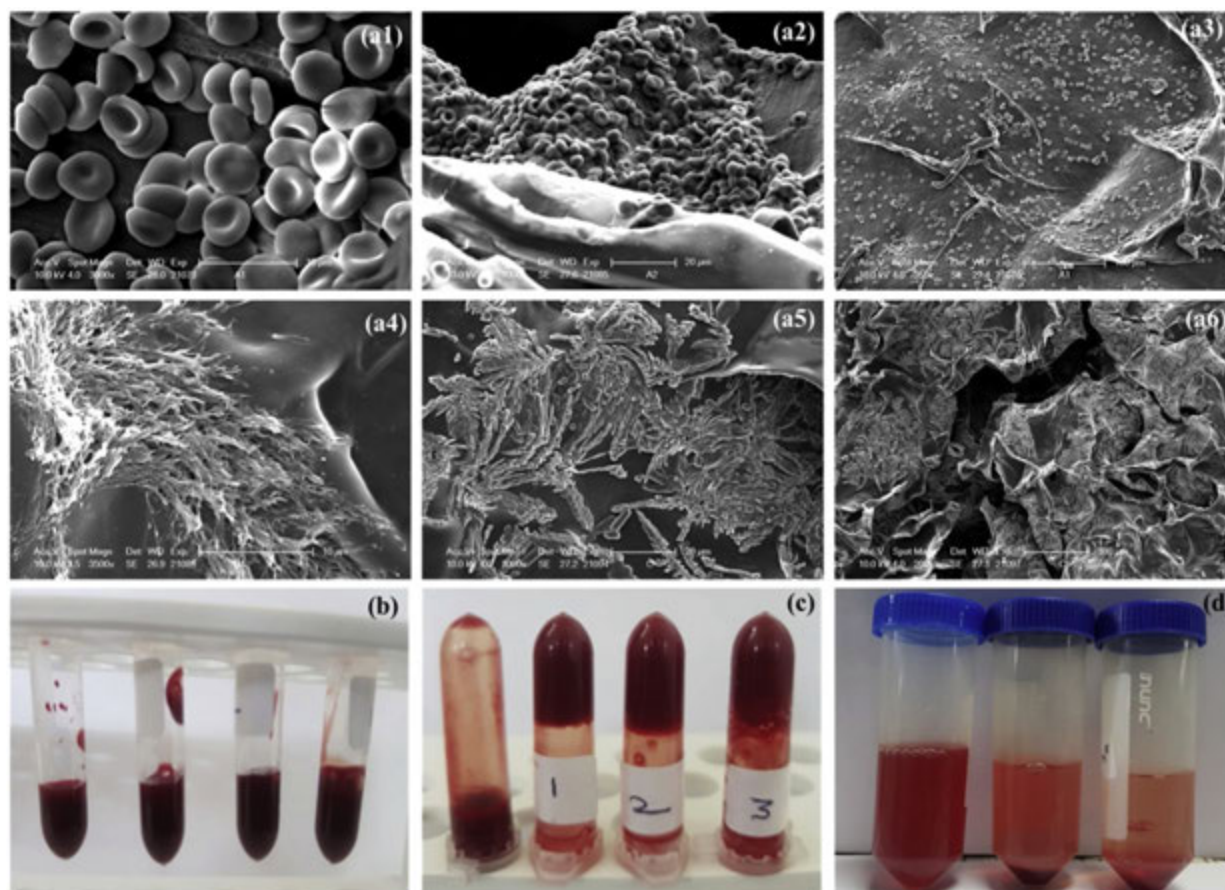


Fig. 1 SEM images of RBCs (a1–a3) and platelets (a4–a6) adhesion on composite dressing at different magnification after incubation of 30 min (a), photographs of tube containing fresh blood without any composite dressing (b), blood clotted with the dressing incubated for 5 min (1), 10 min (2) and 15 min (3) (c), and RBCs leaked from composite dressing for time period of 5 min, 10 min and 15 min (d). (Data points: mean $\pm$ SD and $n = 3$). Reprinted with permission from Biranje, S.S., Madiwale, P.V., Patankar, K.C., *et al.*, 2020. Cytotoxicity and hemostatic activity of chitosan/carrageenan composite wound healing dressing for traumatic hemorrhage. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 239. Elsevier, 116106.

pH = 1.2 but 46.7% at pH = 5.5 in 25 h). The micro-composites containing the greatest CS amount exhibited the most adhered onto the intestinal mucosa after 3 h ($89 \pm 1.79\%$). Some dental restorative composite resins were developed using CS and CS loaded by anhydrous calcium phosphate particles (0, 0.5, 1.0 wt%) indicating antimicrobial activities against *Streptococcus mutans* without losing their biocompatibility and mechanical characteristics (Tanaka *et al.*, 2020). Composite scaffolds of CS and chondroitin sulfate (CTS) containing bioglass nanoparticles were prepared using polyelectrolyte complexation method for application in bone tissue engineering (Singh *et al.*, 2019). The *in vitro* cellular cytotoxicity, viability, spreading and adhesion were assessed in order to estimate the scaffolds effects. Also, the expression of collagen type I, biomineralization and alkaline phosphatase activity were considerably greater on the composite CS scaffold demonstrating its enhanced osteogenic capacity. Moreover, the *in vivo* iliac crest bone defect investigation proved that the implanted composite scaffold facilitated integration with the native bone tissue and assisted the tissue regeneration. A biocompatible composite of CS and carrageenan was achieved as wound dressing to be used in healing of traumatic hemorrhage (see Fig. 1; Biranje *et al.*, 2020). A composite of CS and doxorubicin was electrochemically deposited onto the Ti alloy coated by the hydroxyapatite to decrease the side effects of sustained drug release localized nearby the tumor tissue with the aim of cancer inhibition/apoptosis (Lai *et al.*, 2019). A multifunctional composite food packaging coating indicating biodegradable, transparent, antibacterial and antifogging features was produced using CS modified with a quaternary ammonium salt and poly(vinyl alcohol) by the simple environmentally benign solution casting process (Min *et al.*, 2020). A multifunctional nanocomposite was achieved using hybrid gold/iron oxide nanoparticles that were conjugated to the methotrexate and coated by oleyl CS for application as a dual acting material in the magnetic resonance imaging, MRI, and computed tomography, CT (Hemalatha *et al.*, 2018). Some hydrogels were developed based on the CS, carboxymethyl cellulose (CMC) and hydroxyapatite loaded by different amounts of thyroxine (0.1, 0.5 and 1 $\mu\text{g/mL}$) to improve the angiogenesis in the *in vivo* assays (Malik *et al.*, 2020). The angiogenic activities of the hydrogels were established using the chick chorioallantoic membrane test and it was shown that the hydrogel composed of 0.1 $\mu\text{g/mL}$ thyroxine had the highest neovascularization. Also, the

cytotoxicity test using MC3T3-E1 preosteoblast cells seeded onto the hydrogels confirmed that these materials with the pro-angiogenic capacity were not toxic and suitable for the periodontal regeneration.

It is known that the Gd/Mn containing small molecules used as the MRI contrast agents are not very stable during the extended monitoring and safe if high and repeating doses of them are administered. Hence, a macromolecular biocompatible MRI contrast agent was synthesized using O-CMCS and CMCS-(Mn-DTPA)_n (Wang *et al.*, 2019a). It was found that the CMCS-(Mn-DTPA)_n had a relaxation time that was nearly 5.5 and 3.5 times greater compared to those of the Mn-DPDP and Gd-DTPA within the aqueous environment, respectively (Fig. 2). The intensity of the MRI signals were highly enhanced within the liver and kidney of Sprague Dawley rats using 0.03 mM of Mn/kg b.w. (Fig. 3). The *in vivo* tests approved that Mn was fully excreted from the Sprague Dawley rats in ten days post administration so that it did not exert any pathological effects on their livers. Nanoparticles of core-shell metal organic framework/carbon dots@O-CMCS, were obtained for application in the *in vitro* dual mode imaging, diagnosis, pH-responsive drug delivery and cancer therapy (Lin *et al.*, 2020). The O-CMCS hydrogel conjugated by caffeic acid in addition to its composite with polyacrylamide were developed by means of electron beam irradiation and utilized as antibacterial wound dressings that could deliver doxycycline antibiotic drug (Hafezi Moghaddam *et al.*, 2020). Composite hydrogels of CMCS comprised of hydroxylated lecithin-iodine, HLI, complexes and sodium alginate were prepared using microwave drying method and used in treatment of the infected burn wounds which displayed extraordinary repairing efficacies on the seawater immersed infected wound in rats with deep partially thick burns, see Figs. 4 and 5 (Chen *et al.*, 2019).

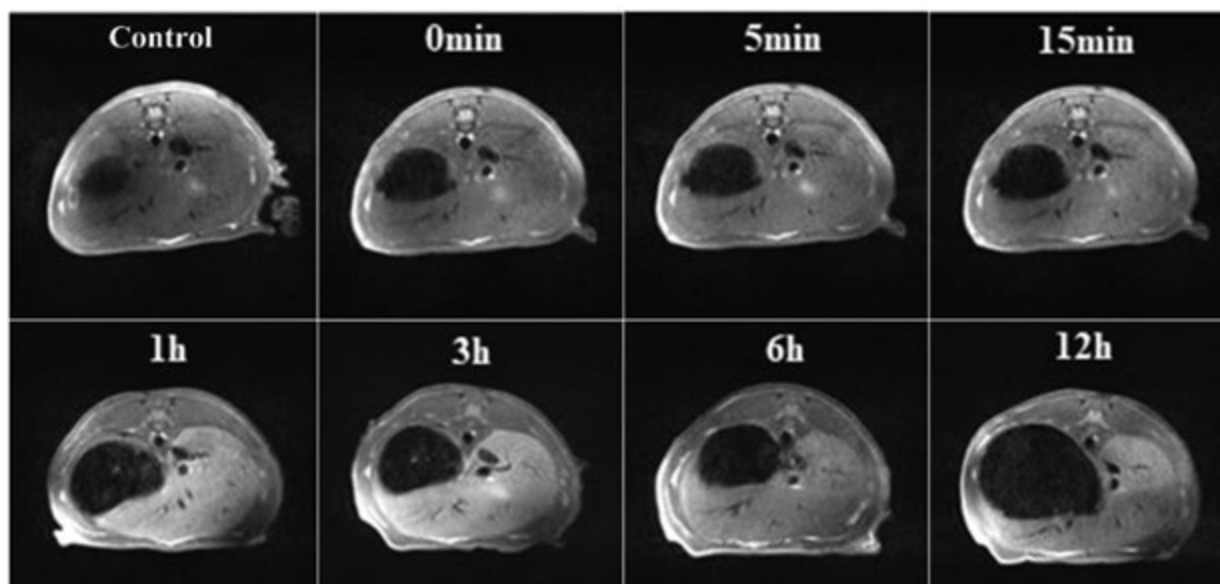
The biological, antibacterial and mechanical characteristics of alginate composite scaffolds were improved through incorporation of magnesium and bioactive zinc containing bioglass that illustrated bactericidal activities (Fig. 6) and were effectively utilized in bone tissue engineering using MG-63 cells (Fig. 7; Zamani *et al.*, 2019). A magnetic bio-inspired hydrogel was fabricated using alginate, gelatin and magnetic Fe₃O₄ nanoparticles, which was employed as a smart and effective drug carrier in cancer treatment against HeLa cells (Jahanban-Esfahlan *et al.*, 2020). A pH-sensitive drug delivery vehicle was fabricated using graphene oxide modified with protamine sulfate as a natural peptide and sodium alginate using the layer-by-layer self-assembly for the delivery of anticancer drug, doxorubicin hydrochloride (Xie *et al.*, 2018). The osteogenic capacity of a composite prepared using poly(vinyl pyrrolidone) and silicate and lanthanum (SiO₄⁴⁻ and La³⁺) substituted hydroxyapatite (synthesized using the calcium alginate as the template) was tested by coating the composite on the surface of a titanium, Ti, implant (Barros *et al.*, 2020).

The effectiveness of HA and poly-D,L lactic acid was explored on the fixation of implants coated the granules of beta-tri-calcium phosphate/hydroxyapatite by a clinical *in vivo* test on sheep which indicated formation of the fresh bones in all groups (Andreassen *et al.*, 2017). The hydrophobic and unstable D- α -tocopherol succinate, α -TOS, was encapsulated inside the pores of zeolitic imidazolate framework-8, ZIF-8, called α -TOS@ZIF-8, and then coated by the HA shell to achieve the HA/ α -TOS@ZIF-8 nanomaterial which was used for the antitumor treatments against human cervical carcinoma, HeLa, cells *in vitro* and U14 uterine cervical tumor bearing mice *in vivo*, see Figs. 8–10 (Sun *et al.*, 2019a). CS/HA sponge composite scaffolds containing andrographolide lipid nanocarriers were fabricated as wound dressing materials which exhibited wound healing in rats without leaving scars (Sanad and Abdel-Bar, 2017). Recently, an electrodeposition layer of Ce(NO₃)₃ · 6H₂O was formed onto the magnesium, and HA was coated by the hydrothermal method to form a polymeric composite layer containing cerium materials plus a stable thick layer of MgO (Kim *et al.*, 2020). Application of this composite on the osteoblasts illustrated their cell viability and non-toxicity to Ce and maximum differentiation particularly using the hydrothermally coated HA. Furthermore, implantation in rat tibias revealed the constant growth of osteoblast and bone marrow using the hydrothermally coated HA. Therefore, CeO₂ and Ce(OH)₃ penetrated into the HA polymer and caused a self-healing capacity, primary corrosion resistance, biodegradation and localized damage of the magnesium implant.

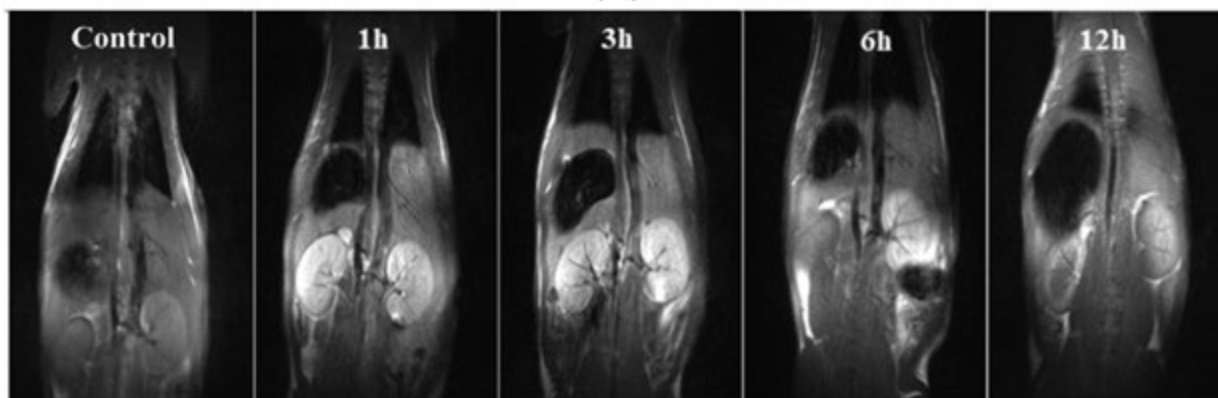
Medical Applications of Cellulose, Carboxymethyl Cellulose, Hydroxyethyl Cellulose and Chondroitin Sulfate Composites

Cellulose, carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and chondroitin sulfate (CTS) are biopolymers with outstanding properties such as nontoxicity, sustainability, biocompatibility, biodegradability, low cost and hydrophilicity that make them appropriate materials for biomedical applications.

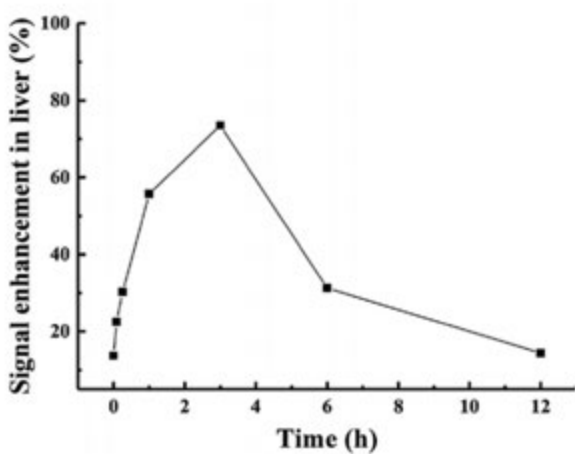
Nanocomposite of cellulose nanocrystals and ultra-small Fe₃O₄ superparamagnetic nanoparticles could be used as a dual negative and positive T₁ and T₂ MRI contrast agent with large saturation magnetization of 52.2 emu/g, high relaxation parameters (r₁ and r₂ were 13.8 and 96.2 mM⁻¹ s⁻¹) plus suitable r₂/r₁ of 7.0 at 3.0 T (Torkashvand and Sarlak, 2019). The nanocomposite displayed satisfactorily *in vitro* cell uptake, *in vitro* low toxicity (200 μ g/mL Fe) against HeLa cells, exceptional biocompatibility and colloidal durability confirming it was a favorable material for application in the medical areas. Some electrospun heparin-like nanofibrous membranes were fabricated using CMCS and bacterial cellulose sulfate demonstrating thrombin, prothrombin and activated partial thrombin times of 48.4, 16.2 and 67.4, respectively, that were 50%, 189.8% and 116.0% greater compared to those of the plasma (Song *et al.*, 2018). Bacterial cellulose/CS scaffolds were attained to be employed in ovarian cancer diagnosis through the interaction of scaffolds with the A2780 ovarian cancer cells (Ul-Islam *et al.*, 2019). A biodegradable composite gauze was prepared by means of N, O-CMCS and oxidized regenerated cellulose that was utilized as a wound dressing barrier to prevent the postoperative adhesion and illustrated antibacterial activities against *E. coli* and *S. aureus* microorganisms (Cheng *et al.*, 2019). Bacterial cellulose scaffolds modified with alginate and incorporated with different amounts of doxorubicin drug were achieved for the local release of doxorubicin in HT-29 human colorectal cells that displayed 53%–95% loss in viability of cells after 24 h and



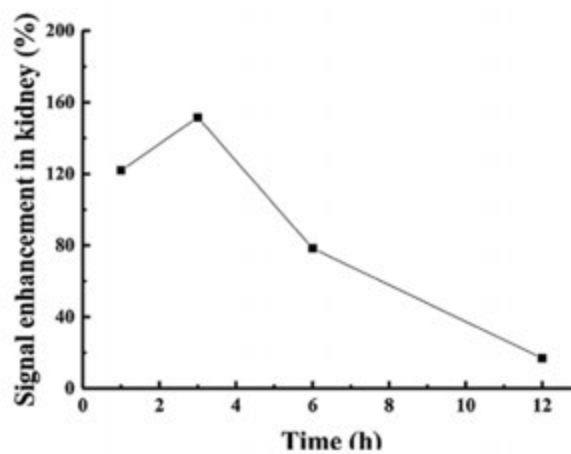
(A)



(B)



(C)



(D)

Fig. 2 *In vivo* T1-weighted MRI images of the rat liver (A) and kidney (B) before and at different time points (0 min, 5 min, 15 min, 1 h, 3 h, 6 h and 12 h) after the intravenous injection of CMCS-(Mn-DTPA)_n at a dose of 0.03 mM Mn/kg b.w. The signal enhancement (SE) rate in the rat liver (C) and kidney (D) changed over time after the injection. Reprinted with permission from Wang, X., Xu, L., Ren, Z., *et al.*, 2019a. A novel manganese chelated macromolecular MRI contrast agent based on O-carboxymethyl chitosan derivatives. *Colloids and Surfaces B: Biointerfaces* 183, 110452.

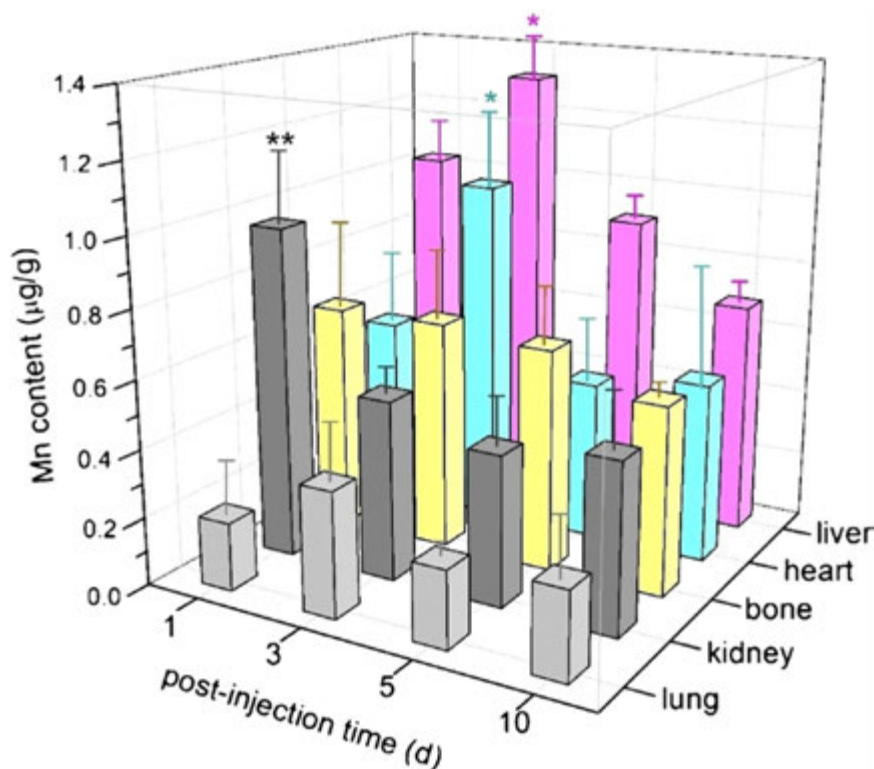


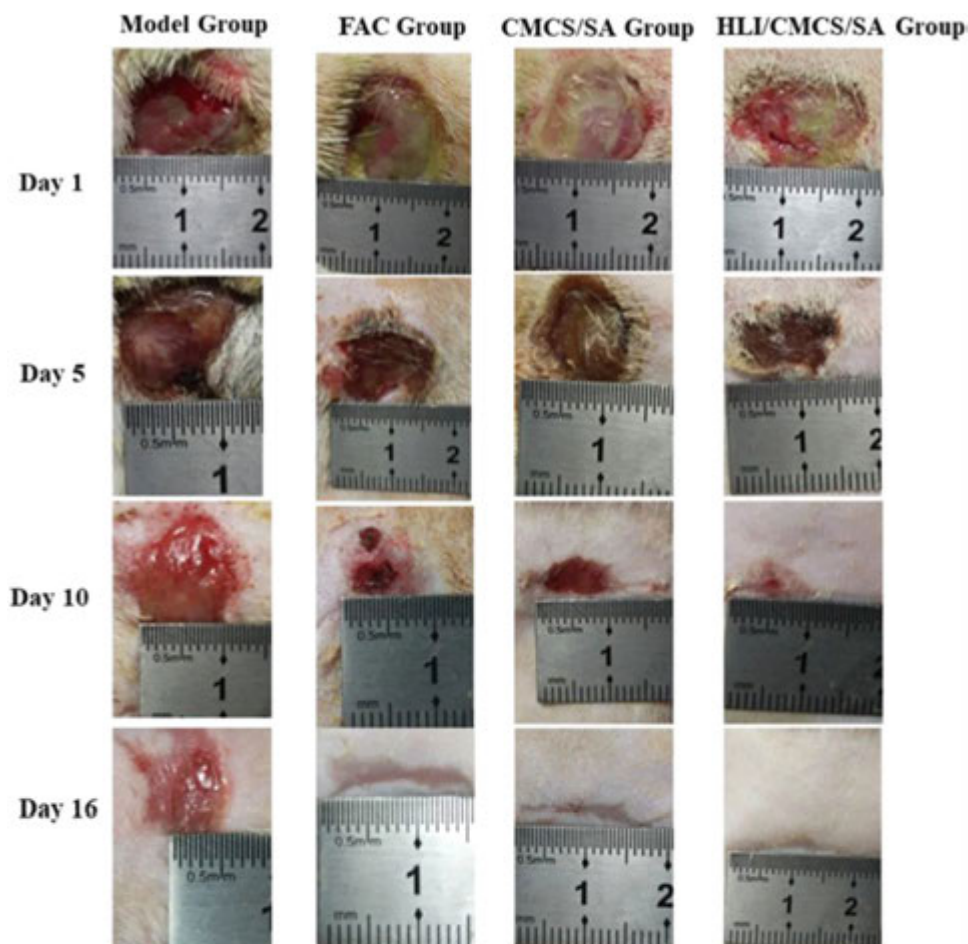
Fig. 3 Mn contents in different organs at different time points after CMCS-(Mn-DTPA)_n injection at a dose of 0.03 mM Mn/kgb.w.(means $\pm$ SD, n=4). *P<0.05 and **P<0.01 compared to the control group. Reprinted with permission from Wang, X., Xu, L., Ren, Z., *et al.*, 2019a. A novel manganese chelated macromolecular MRI contrast agent based on O-carboxymethyl chitosan derivatives. *Colloids and Surfaces B: Biointerfaces* 183, 110452.

37%–63% after 48 h (Cacicedo *et al.*, 2016). The core-shell nanoparticles were fabricated using Fe₃O₄ core coated by the hydrogel shell that was dually encapsulated with both hematoporphyrin monomethyl ether and doxorubicin and then conjugated with the folic acid which was grafted to the composite surface and introduced in the bacterial cellulose membrane (Zhang *et al.*, 2019). On the day 14 post treatment, the tumor growth inhibition was 80.38%. The transdermal delivery of the composite to the breast cancer cells was done by applying laser and a magnetic field and low penetration depth was happened which enhanced the transdermal delivery of drugs and facilitated the bypass by the stratum corneum barrier.

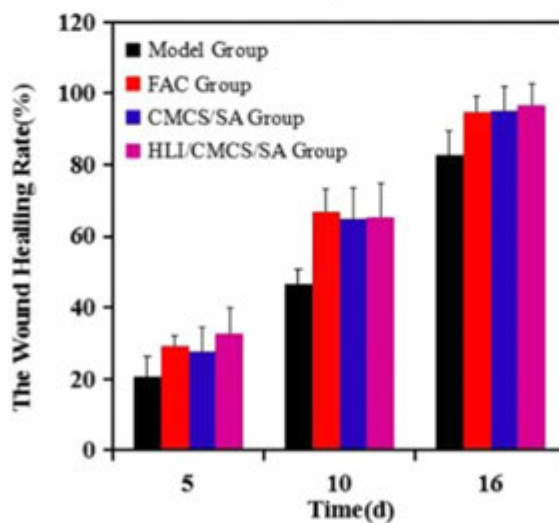
Composite microbeads of Fe₃O₄@C/CMC/CS were we produced as a dual magnetic and pH responsive formulation and used in controlled delivery of diclofenac sodium to the gastrointestinal tract without burst release (Sun *et al.*, 2019b). Several hydrogel composite films were fabricated using CS microspheres incorporated to the CMC hydrogel as redox responsive systems through cystamine dihydrochloride as a disulfide crosslinker and employed for the co-delivery of 5-fluorouracil anticancer and tetracycline hydrochloride antibiotic drugs (Wang *et al.*, 2019b). A CMC-CMCS-collagen (COL) composite was achieved through crosslinking catalyzed by transglutaminase that was utilized as an anti-adhesion membrane composed of different ratios of CMC, CMCS and COL including 25/25/50, 35/35/30 and 40/40/20 (Figs. 11 and 12; Cai *et al.*, 2018). Porous CS/CMC scaffolds were prepared through freeze drying technique that were reinforced using whisker shaped triphasic and biphasic calcium phosphate fibers and used in bone tissue engineering (Matinfar *et al.*, 2019).

Some composite scaffolds of HEC, sodium alginate and hydroxyapatite were fabricated by crosslinking with the calcium ions the lyophilization process to enhance the *in vitro* regeneration of bone tissue and it was found that they led to proliferation and viability of cell human mesenchymal stem cells *in vitro* (Tohamy *et al.*, 2018). Composite scaffolds of HEC/Ag nanoparticles were produced for the application in skin tissue engineering using hFB human fibroblast cells and it was illustrated that the scaffolds had low toxicity *in vitro* to the cells (Zulkifli *et al.*, 2017). a biocompatible porous scaffold was to developed based on HEC and poly(vinyl alcohol) by the freeze drying procedure which demonstrated enhanced adhesion to the hFB human fibroblast cells and good cell proliferation 7 days post cultivation (Zulkifli *et al.*, 2019). Composite sponges were made using HEC and soy protein isolate that were crosslinked by ethylene glycol diglycidyl ether through the freeze drying technique and revealed satisfactory biocompatibility and adhesion of L929 murine fibroblast cells onto nearly everywhere of their interiors and surfaces confirming they were suitable materials for the tissue engineering (Zhao *et al.*, 2018).

A microporous blend membrane was fabricated as directed bone regeneration based upon the strontium CTS and silk fibroin, called SrCTS/SF, and it was displayed that its water retention capability and mechanical characteristics as well as proliferation of the osteoblasts were improved by increasing the SrCTS content (Fenbo *et al.*, 2019). A biodegradable self-crosslinked and *in situ*



a



b

Fig. 4 Morphologies (a) and healing rates (b) of the wounds treated with different wound dressings during the repairing process. Fusidic acid cream (Fucidin®, FAC) contained 20 mg/g fusidic acid. SA=sodium alginate. Reprinted with permission from Chen, Y., Qiu, H., Dong, M., *et al.*, 2019. Preparation of hydroxylated lecithin complexed iodine/carboxymethyl chitosan/sodium alginate composite membrane by microwave drying and its applications in infected burn wound treatment. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 206. Elsevier, pp. 435–445.

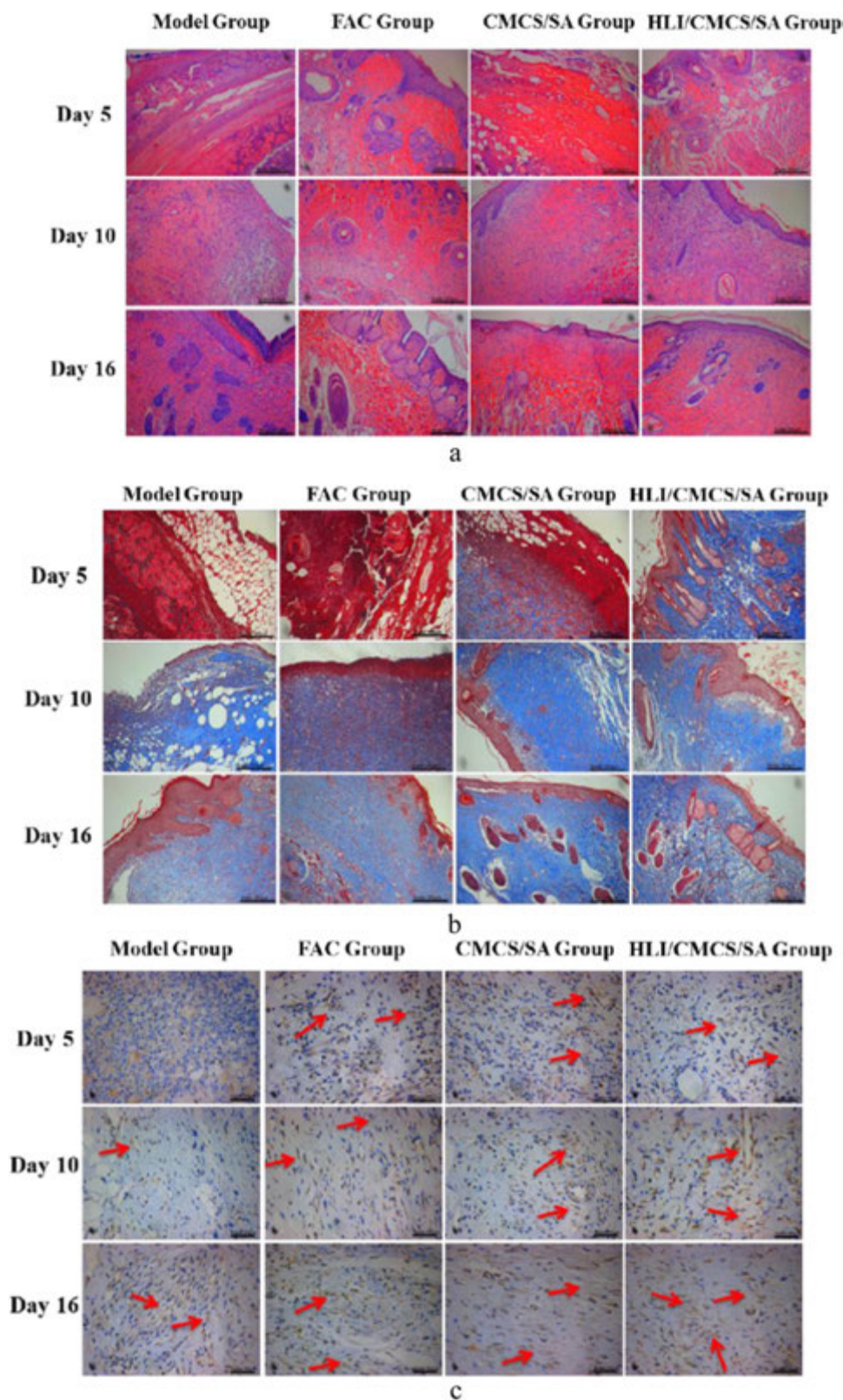


Fig. 5 The histological section images for H.E. staining (a), Masson's staining (b), and immuno-histochemical staining for VEGF ($\times 400$) of the infected wounds treated with different dressings during the repairing process. Reprinted with permission from Chen, Y., Qiu, H., Dong, M., *et al.*, 2019. Preparation of hydroxylated lecithin complexed iodine/carboxymethyl chitosan/sodium alginate composite membrane by microwave drying and its applications in infected burn wound treatment. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 206. Elsevier, pp. 435–445.

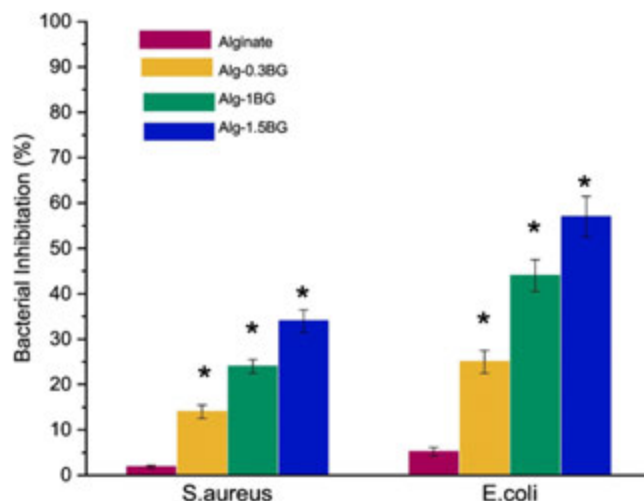


Fig. 6 Antibacterial activities of diverse scaffolds to show the effect of Bioglass including Zn and Mg concentrations on bacterial inhibition. *Different from alginate sample ($p < 0.05$, $n = 3$). Reprinted with permission from Zamani, D., Moztaaradeh, F., Bizari, D., 2019. Alginate-bioactive glass containing Zn and Mg composite scaffolds for bone tissue engineering International. Journal of Biological Macromolecules 137, 1256–1267.

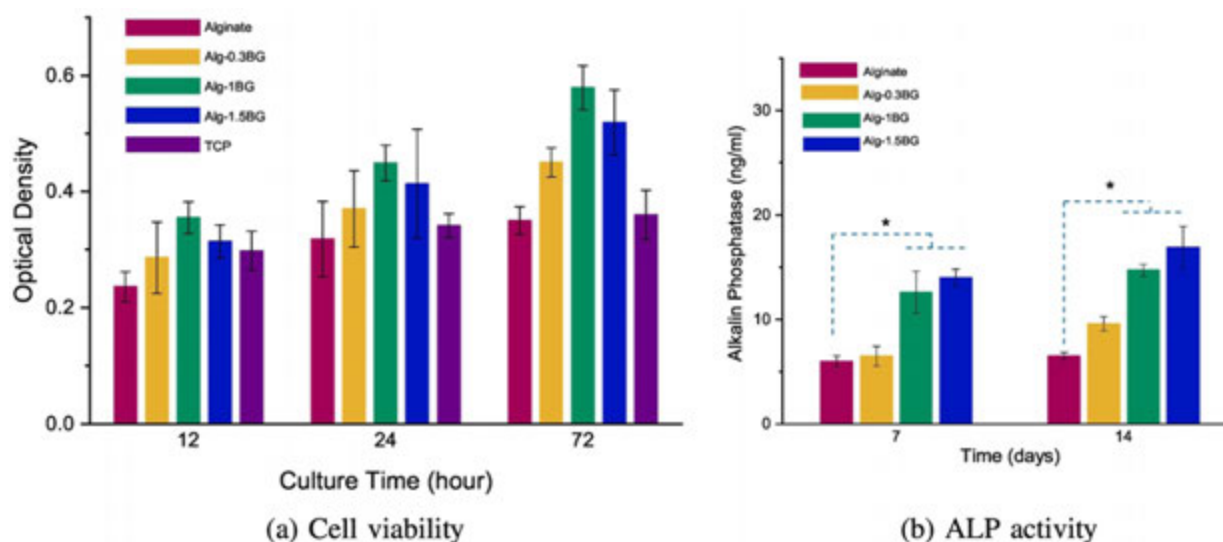


Fig. 7 (a) Cell viability (using MTT assay) and (b) ALP activity of alginate and composite scaffolds using MG-63 cell lines. Reprinted with permission from Zamani, D., Moztaaradeh, F., Bizari, D., 2019. Alginate-bioactive glass containing Zn and Mg composite scaffolds for bone tissue engineering International. Journal of Biological Macromolecules 137, 1256–1267.

formed injectable hydrogel was synthesized using CTS conjugated to adipic dihydrazide, CTS-ADH, and oxidized pullulan, oxPL which was employed in cartilage tissue engineering (Li *et al.*, 2018). It was recognized that the rabbit articular chondrocytes were encapsulated within the CTS-ADH/oxPL hydrogels 14 days post culturing so that the hydrogel was well cytocompatible according to the live/dead staining test and favored deposition of the cartilaginous extracellular matrix as proved by the amount of sulfated glycosaminoglycan. A composite hydrogel resembling cell delivery system was achieved using type II collagen and CTS crosslinked by genipin that was used to deliver the adipose-derived stem cells (Zhou *et al.*, 2018). The biocompatible scaffold induced the *in vitro* differentiation of cells, regenerated *in vivo* the rat coccygeal vertebrae degenerated model by promoting the expression of genes specific to nucleus pulposus. Nanoparticles of CTS A/deoxycholic acid were conjugated to the polyethylene glycol and used in the tumor targeted doxorubicin delivery to the ovarian cancer (Lee *et al.*, 2016). The conjugated nanoparticles revealed endocytosis into the SKOV-3 cells that were CD44 receptor-positive human ovarian cancer cells. A polyelectrolyte complex was prepared based on CTS and CS which formed an *in situ* scaffold that was not hemolytic, suitably blood compatible and exhibited small blood clotting index with satisfactory antibacterial capacity against Gram-negative and Gram-positive microorganisms, appropriate cytocompatibility as well as almost four times enhanced density of L929 fibroblast cells than that of the control confirming it could effectively control the chronic wounds (Sharma *et al.*, 2019).

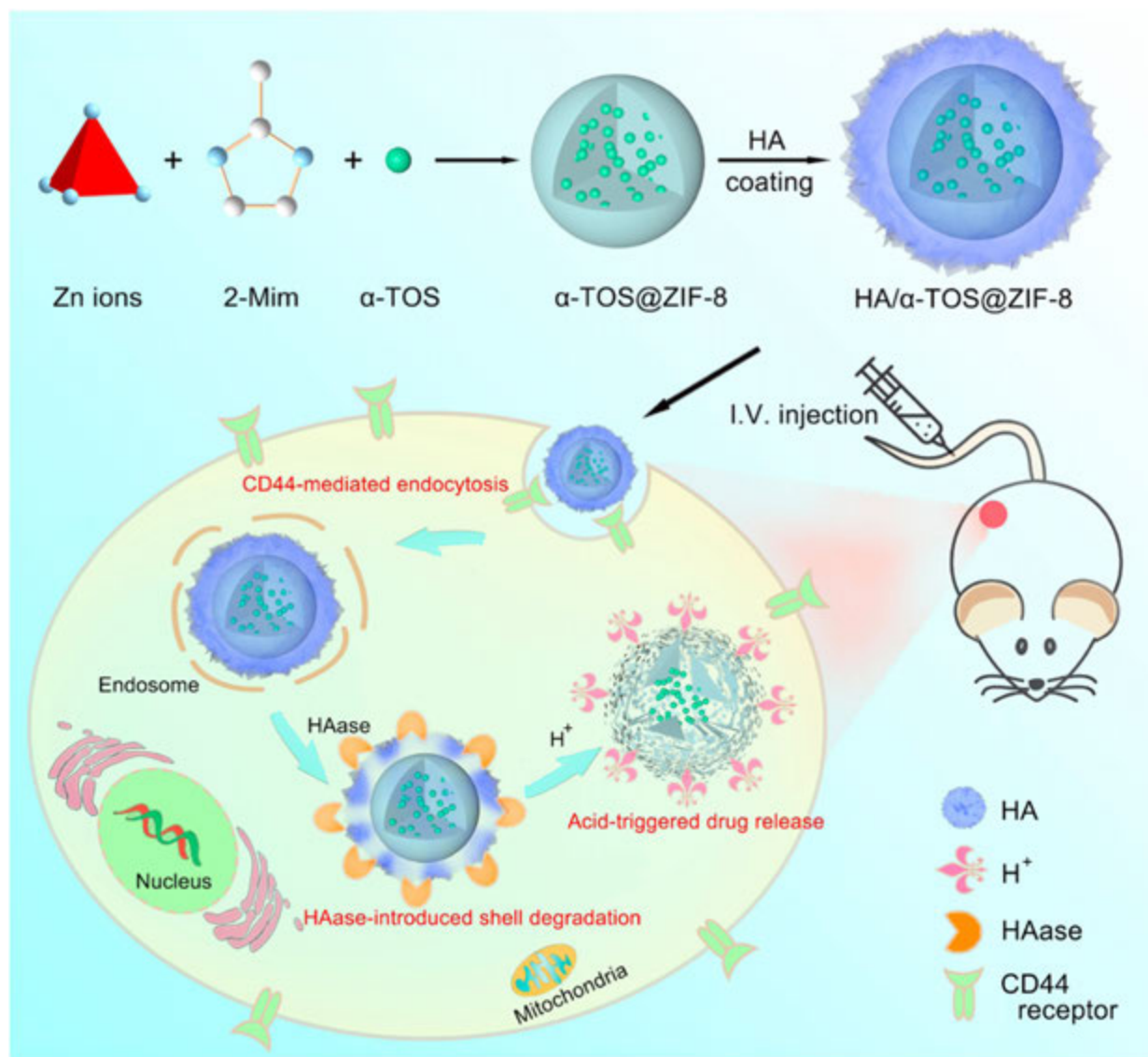


Fig. 8 Schematic illustration for the formation of HA/ α -TOS@ZIF-8 nanoplateform. Schematic illustration showing the CD44 receptors-mediated pH-responsive drug delivery system for efficient antitumor therapy. Reprinted with permission from Sun, Q., Bi, H., Wang, Z., *et al.*, 2019a. Hyaluronic acid-targeted and pH-responsive drug delivery system based on metal-organic frameworks for efficient antitumor therapy. *Biomaterials* 223, 119473.

Medical Applications of Starch, Carboxymethyl Starch, Zein and Gelatin Composites

Starch, carboxymethyl starch (CMS), zein and gelatin (GEL) are famous biopolymers that are frequently applied in various biomedical purposes. Herein, some recent examples are provided to indicate their significance.

Porous composites of starch-HA were fabricated by crosslinking with sodium trimetaphosphate and utilized as hemostatic materials which displayed exceptional blood clotting in superficial injuries, artery trauma and solid viscera and demonstrated a hemostatic efficiency comparable to that of the commercial Quickclean® hemostat particles (Wang *et al.*, 2020). Some hybrid composite gels were generated through the vacuum freeze drying method using a high amylose starch and microcrystalline cellulose that encapsulated the ranitidine hydrochloride drug and used for the gastric floating delivery (Xu *et al.*, 2019). The *in vitro* drug release test indicated that the 3:7 wt/wt% of starch: cellulose gel revealed 45.87% release in the initial 1 h and a then a sustained drug release in 10 h within simulated gastric fluid. A hydrogel micro-composite was prepared based on starch and cellulose nanowhiskers by the ultrasound irradiation and loaded by the vitamin B₁₂ which exhibited a sustained drug release (Mauricio *et al.*, 2015). Starch conjugated graphene nanosheets were obtained as pH sensitive nano-carriers by reducing exfoliated graphene oxide with soluble starch that was served as a functionalization and reducing agent that capped the graphene nanosheets and prevented their aggregation (Liu *et al.*, 2015). The hydroxycamptothecin drug loaded nano-carriers illustrated no cellular to

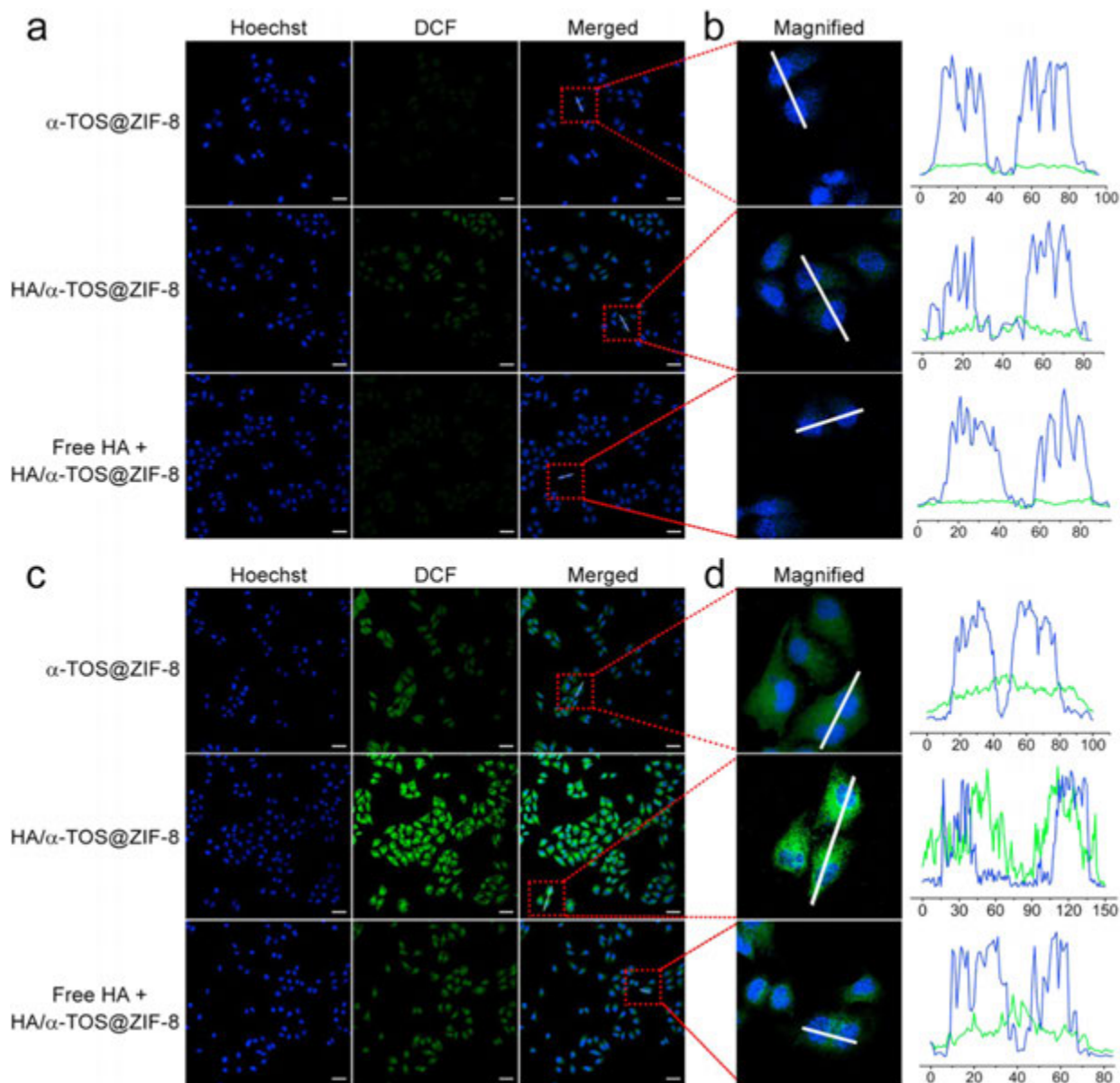


Fig. 9 CLSM images of HeLa cells incubated with α -TOS@ZIF-8, HA/ α -TOS@ZIF-8 and HA/ α -TOS@ZIF-8 in the presence of free HA after (a) 0.5 and (c) 3 h in the dark. Scale bars for all images are 50 μ m. The magnified images from the corresponding merged a and c, and the fluorescence intensity profiles along the white line crossing the cancer cells (b, d). Reprinted with permission from Sun, Q., Bi, H., Wang, Z., *et al.*, 2019a. Hyaluronic acid-targeted and pH-responsive drug delivery system based on metal-organic frameworks for efficient antitumor therapy. *Biomaterials* 223, 119473.

SW-620 cells even using 200 g/mL concentration. Also, they were internalized into the SW-620 cancer cells *via* the non-specific endocytosis influence. At acidic pH and in presence of the diastase enzymes existing within the SW-620 cells, the composite nanocarriers were highly toxic towards the SW-620 cells and depicted a pH responsive and *in vitro* starch assisted sustained release that resulted in improved therapeutic efficiency.

CMS coated superparamagnetic Fe_3O_4 nanoparticles were fabricated for the MRI imaging and also for the controlled delivery of the 5-aminosalicylic acid, mesalamine, drug parenterally administered (Saboktakin *et al.*, 2009). CS and its CMS polyelectrolyte complexes were fabricated as tablets achieved through direct compression method using two diverse grades of CS and different CS: CMS ratios which contained the acetaminophen drug (Leonida *et al.*, 2018). It was found that previous incubation of the tablets into the acidic simulated gastric fluid produced longer dissolution plots with complete drug release during 16 h and maintaining the shapes of tablets but tablets directly exposed into the simulated intestinal fluid were quickly degraded. Nanocomposites of CMS (from Assam Bora rice) coated superparamagnetic Fe_3O_4 nanoparticles were synthesized and localized *in vitro* inside micro capillaries to simulate targeted drug vehicles responding to the applied external magnetic field (Mohapatra *et al.*, 2018).

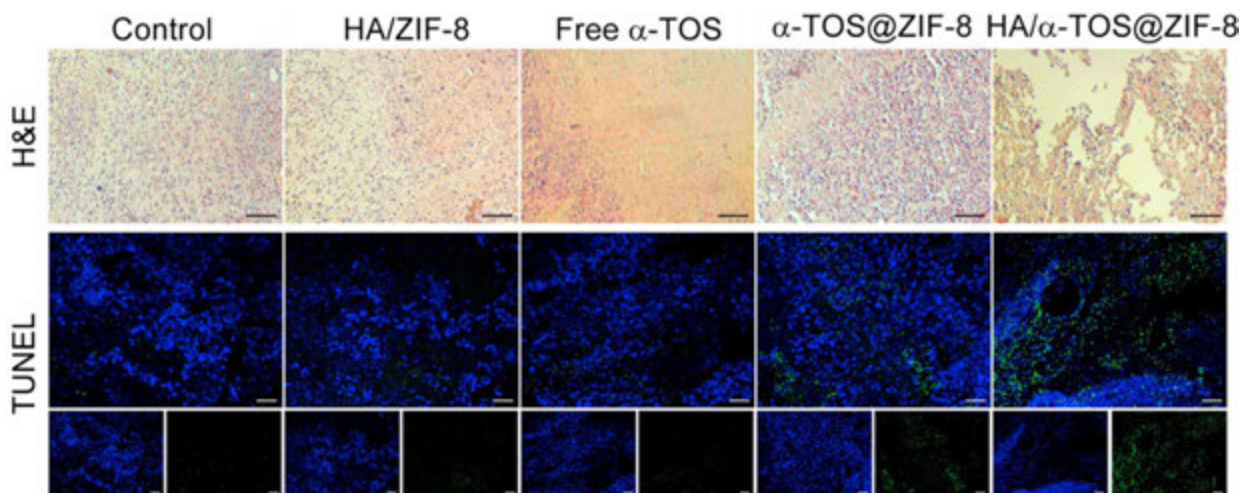


Fig. 10 Hematoxylin and eosin (H&E) and terminal deoxynucleotidyl transferase mediated dUTP-biotin nick end labeling assay (TUNEL) images of tumor tissues from mice after different treatments on the 14th day (scale bar: H&E 56 μm , TUNEL 50 μm). Reprinted with permission from Sun, Q., Bi, H., Wang, Z., *et al.*, 2019a. Hyaluronic acid-targeted and pH-responsive drug delivery system based on metal-organic frameworks for efficient antitumor therapy. *Biomaterials* 223, 119473.

A biodegradable, biocompatible and hemostatic formulation was produced through modification of CMS by calcium ions to achieve freely flowing micro-particles indicating enhanced clotting effects approved by the *in vivo* and *in vitro* assays (Figs. 13 and 14; Panwar *et al.*, 2019). Microparticles of CMS/CS polyelectrolyte complexes were achieved as drug carriers encapsulated the bovine serum albumin that exhibited pH sensitive *in vitro* drug release in both of the simulated intestinal fluid and simulated gastric fluid with pH values of 6.8 and 1.2, respectively (Quadrado and Fajardo, 2020).

Nanofibrous electrospun zein mats (diameters of ~ 350 – 500 nm) incorporated with the Ag nanoparticles (~ 20 nm) were concurrently were fabricated as wound dressing materials and revealed high bactericidal activities against Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria (Dashdorj *et al.*, 2015). Several electrospun fibrous and antibacterial scaffolds were achieved by three different electrospinning approaches (suspension, multilayer and two-nozzle electrospinning) based on poly(ϵ -caprolactone), zein and gum arabic encapsulated with *Calendula officinalis* extract that is a significant therapeutic plant generally utilized to treat skin injuries like cuts, burns, rashes, foot ulcer and bruise (Pedram Rad *et al.*, 2019). It was shown that the scaffolds containing *Calendula officinalis* extract exhibited greater bactericidal capacities than those fabricated without adding the extract confirming they were appropriate for the skin tissue engineering. electrospun nanofiber mats were produced by zein and cellulose acetate and loaded with sesamol antioxidant to assist the wound healing process to examine the influences of sesamol incorporated nanofibrous composite mats onto the wound healing in diabetic mice (Liu *et al.*, 2020). It was indicated that the nanocomposite mat contained a high dose of 5% sesamol relative to the total polymer weight, could induce the myofibroblasts creation through enhancement of the TGF- β signaling path transduction. Also, it stimulated the growth of keratinocytes through inhibition of the chronic inflammation within the wounds and led to improved healing of wounds in diabetic mice. Some macroporous composite scaffolds were prepared as anti-infective, antibacterial, biodegradable and osteo-inductive materials to enhance the bone tissue regeneration using SBA-15 nanoparticles, zein and hydroxypropyltrimethyl ammonium chloride CS, HACC, that were encapsulated by rhBMP-2 to deliver osteogenic factors and expedite efficient repairing the bone defects, see Fig. 15 (Zhou *et al.*, 2014). Zein/HA nanoparticles were obtained using sodium hyaluronate (100 kDa) to deliver the anticancer drug curcumin (loading capacity and encapsulation efficiency were 3.66% and 95.03%, respectively) that displayed a high resistance to the photodegradation and controlled drug release within the simulated gastrointestinal fluid (Chen *et al.*, 2018).

Antibacterial and hemo-compatible wound dressings were achieved based on the composite hydrogels prepared from konjac glucomannan and fish gelatins and encapsulated with the matrine, as a Chinese herbal medicine (Zhou *et al.*, 2020). It was found that using 40 mg/mL of matrine afforded bactericidal inhibition zones 11.5 and 12 mm for the *S. aureus* CMCC(B) 26003 and *E. coli* ATCC25922 bacteria, respectively. Antibacterial and natural wound dressing materials were fabricated using composite sponges of GEL and bacterial cellulose which exhibited exceptional antimicrobial activities against *S. aureus*, *C. albicans* and *E. coli* microorganisms (Ye *et al.*, 2019). To enhance the viability of cryopreserved SaOS-2 cells, porous biocompatible hydrogel composites were developed using blended GEL, sericin and carrageenan loaded by several growth factors and drugs which were utilized in bone regeneration treatments and exhibited enhanced cell attachment and cryopreservation (Ashe *et al.*, 2020). Alendronate, insulin like growth factor, IGF-1, and Ag nanoparticles were separately introduced in the hydrogels and it was shown that the IGF-1 containing composite hydrogel had superior osteogenic cell revival, proliferation and attachment during the cryopreservation along with 55% clonogenic capacity for the seeded SaOS-2 cells and 80% population of live cells in 30 days cryopreservation confirming this hydrogel was a promising material for regeneration and repairing of bones. Several three-dimensional bioprinting composite hydrogels by extrusion method using GEL and alginate hydrogels crosslinked by 2 wt% of CaCl_2 and encapsulated with

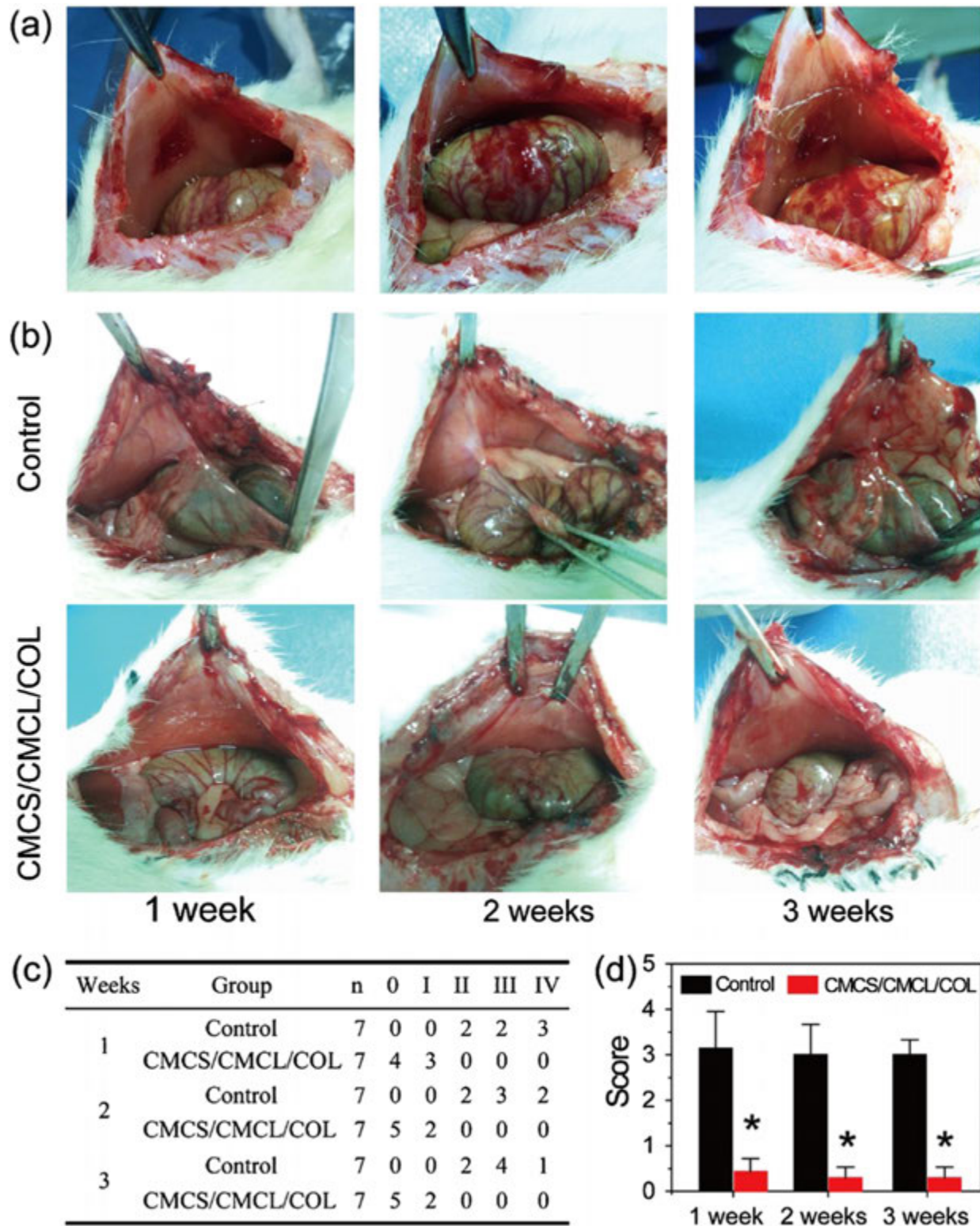


Fig. 11 (a) Photograph of the surgical site during the operation. Defect on the abdominal wall (left) and the cecum outer wall (middle). Photograph of anti-adhesion membrane implanted on the injured abdominal wall and cecum outer wall (right). (b) Photographs of peritoneal adhesion after surgery 1 week, 2 weeks, and 3 weeks. Peritoneal adhesion (c) grades and (d) scores for control and test group (* $P < 0.05$ versus the control group). Reprinted with permission from Cai, X., Hu, S., Yu, B., *et al.*, 2018. Transglutaminase-catalyzed preparation of crosslinked carboxymethyl chitosan/carboxymethyl cellulose/collagen composite membrane for postsurgical peritoneal adhesion prevention. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 201, Elsevier, pp. 201–210.

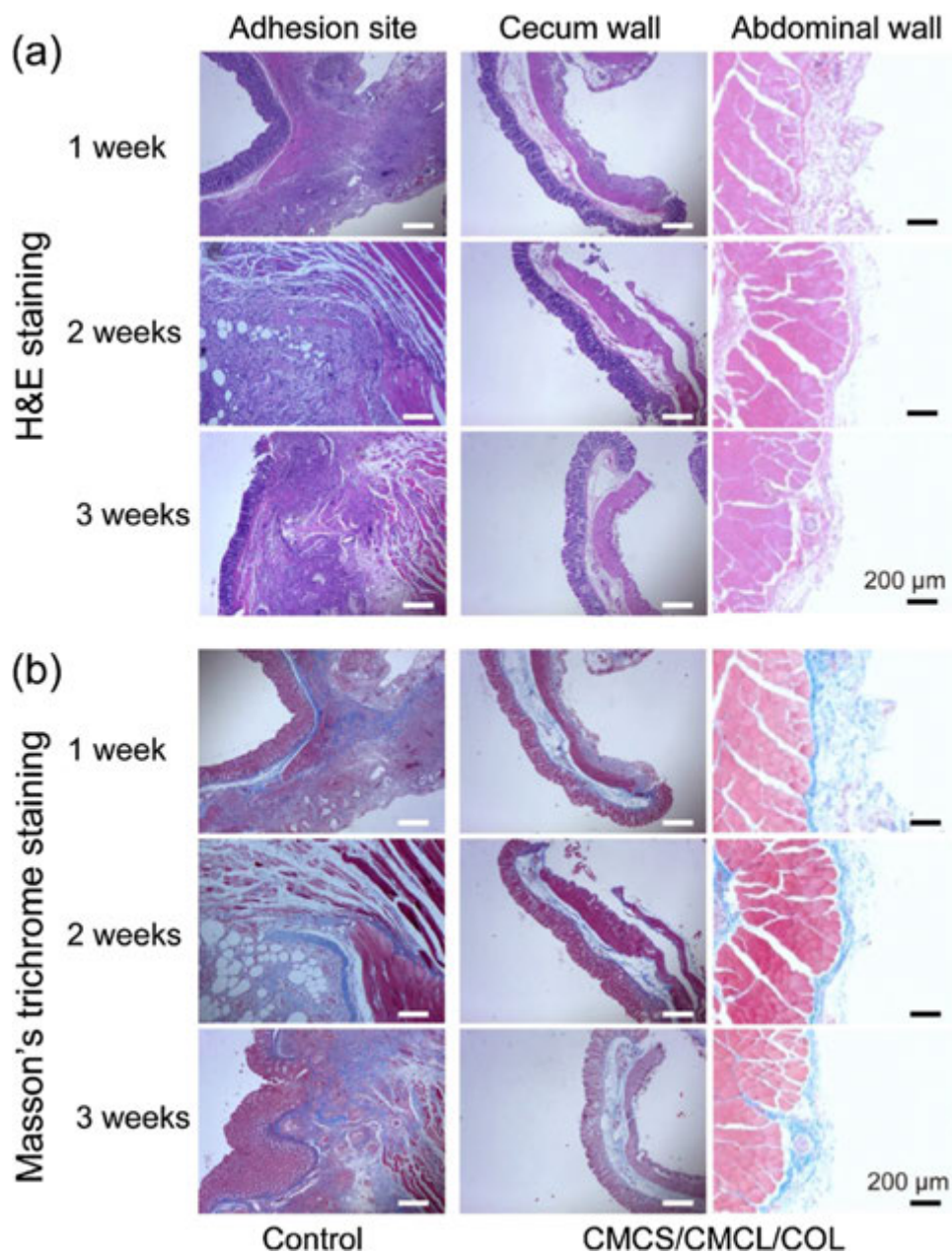


Fig. 12 Histological observation of rat peritoneal adhesion by (a) H&E staining and (b) Masson's trichrome staining. In H&E staining, nucleus was blue, while muscle fibers and cytoplasm were red. In Masson's trichrome staining, collagen fibers were blue, while muscle fiber, cellulose and red blood cells were red. Reprinted with permission from Cai, X., Hu, S., Yu, B., *et al.*, 2018. Transglutaminase-catalyzed preparation of crosslinked carboxymethyl chitosan/carboxymethyl cellulose/collagen composite membrane for postsurgical peritoneal adhesion prevention. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 201, Elsevier, pp. 201–210.

human amniotic epithelial cells and Wharton's jelly derived mesenchymal stem cells to be used in regenerative medicine and skin tissue engineering (Liu *et al.*, 2019). It was illustrated that the GEL: alginate ratio of 15:2 wt%: wt% for bioprinting the constructs such as ear and nose afforded high bioprinting resolution of $151 \pm 13.04 \mu\text{m}$ at low temperature of 4°C . Also, high cellular viability of $>95\%$ was measured in 6 days post bioprinting. Some gene delivery systems were fabricated using bioactive electrospun GEL scaffolds loaded with plasmid DNA, pDNA, polyplexes capable of gene expression (Pankongadisak *et al.*, 2020). To prepare the pDNA, polyplexes, the pDNA was mixed with lipid conjugated polyethylenimine to attain polyplexes (size = 82 nm) containing poly(aspartic acid), pAsp, as an additive. The pDNA polyplexes displayed considerably greater transfection capacities within solution as well as when they were entrapped into the electrospun scaffolds according to the GFP expression in the MC3T3-E1 mouse osteoblast and C2C12 human myoblast cells. The gene triggered activities of mats were validated using a pDNA encoded BMP-2 that showed strong induction of alkaline phosphatase within the MC3T3-E1 and C2C12 cells approving their osteogenic

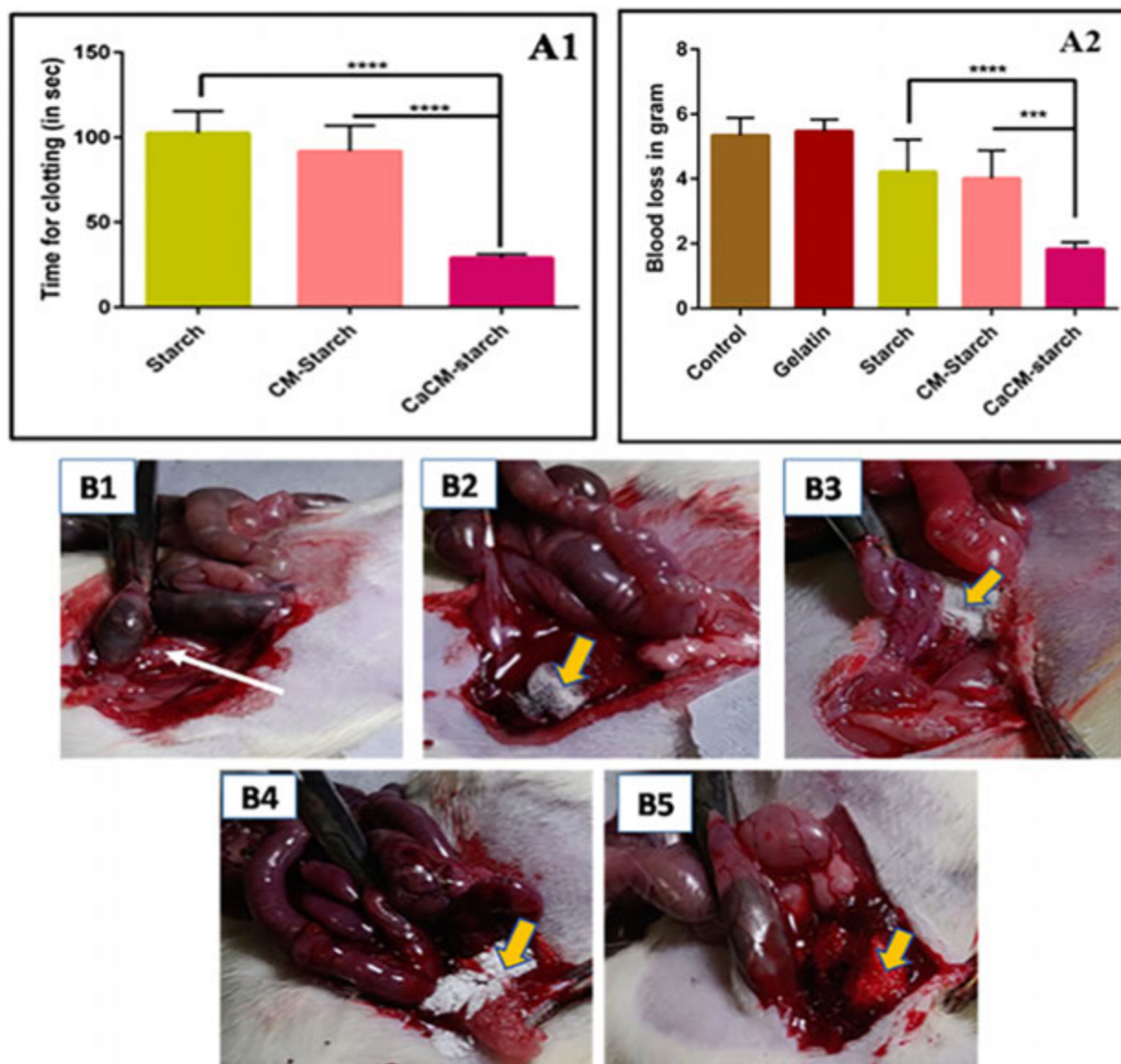


Fig. 13 Hemostasis in rat abdominal aorta injury. A1) Time for clotting in control rats and gelatin foam-treated rats are not shown as no clotting was observed and the animals died of bleeding. A2) Blood Loss. ****indicates $p \leq 0.0001$. Data is represented as mean $\pm$ SD ($n=6$); Images show hemostatic response in rat abdominal aorta injury. B1) Control (White arrow shows the injured vessel); B2) Gelatin; B3) Starch; B4) CM-Starch and B5) CaCM-Starch respectively (Yellow arrow points to the respective treatment's). Data is represented as mean $\pm$ SD ($n = 6$). Reprinted with permission from Panwar, V., Sharma, A., Thomas, J., *et al.*, 2019. In-vitro and In-vivo evaluation of biocompatible and biodegradable calcium-modified carboxymethyl starch as a topical hemostat. *Materialia* 7, 100373.

differentiation. Thus, the GEL fibrous mats composed of bioactive pDNA polyplexes were appropriate materials for regenerative repairing numerous tissues. Actuation hydraulic device were fabricated using GEL phantoms which caused 1 Hz motions to investigate the image reconstruction by the intrinsic actuation-magnetic resonance elastography (Gordon-Wylie *et al.*, 2018).

Medical Applications of Gellan Gum, Acacia Gum, Guar Gum, Tamarind Gum and Xanthan Gum Composites

There are numerous gums that are broadly employed in biomedical applications including gellan gum (GG), acacia gum (AG), guar gum (GUG), tamarind gum (TG) and xanthan gum (XG). These materials are natural polysaccharides which can be fabricated as composites in order to improve their physicochemical and structural properties to be satisfactory for the clinical and medical applications. In the following, several biomedical applications of such composite gums are presented.

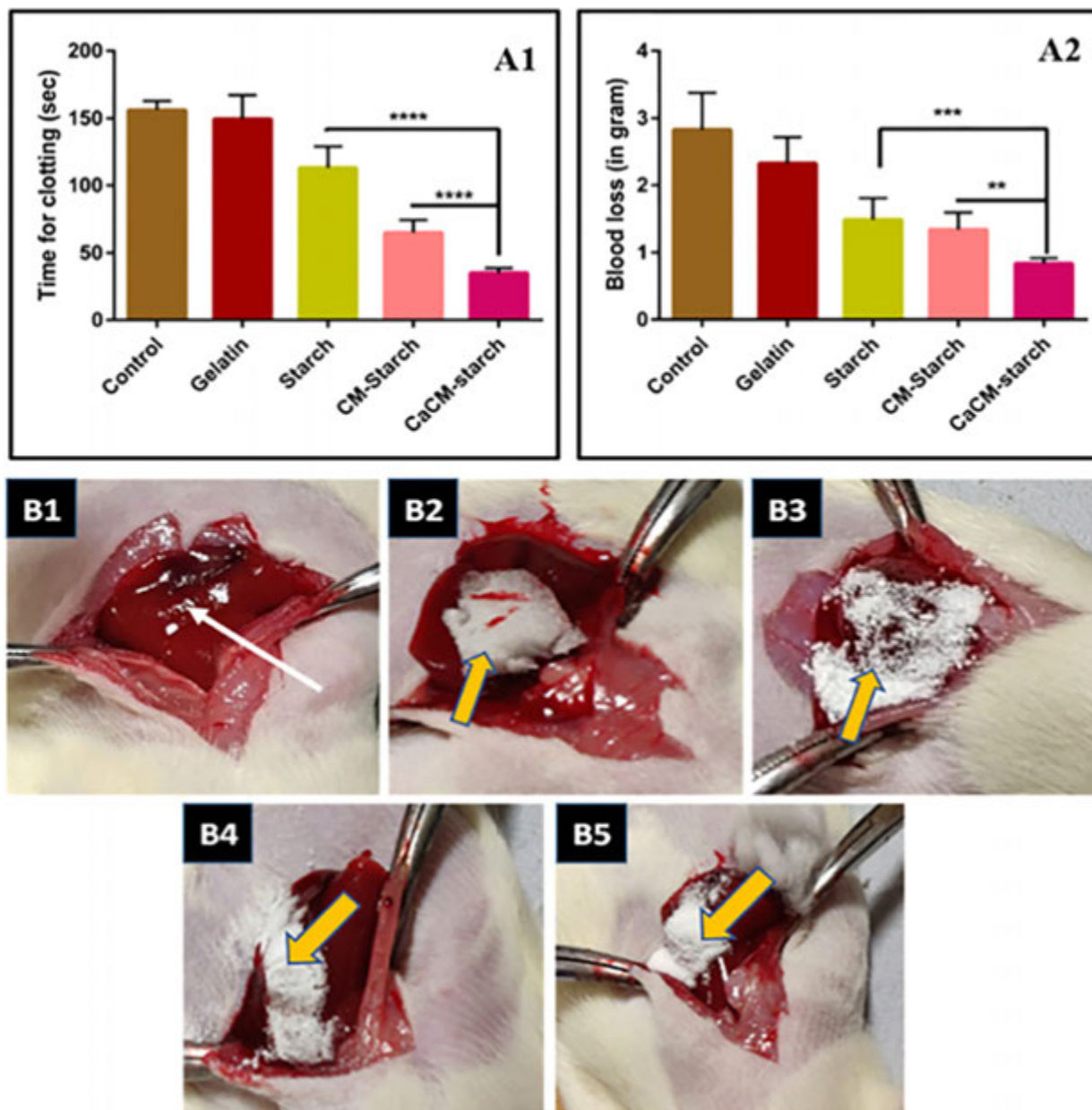


Fig. 14 Hemostasis in rat liver injury (A1) time for clotting; (A2) blood Loss. ****indicates $p \leq 0.0001$. Images show hemostatic response in rat liver injury following various treatments (B1) Control (white arrow shows the injured site); (B2) Gelatin; (B3) Starch; (B4) CM-Starch and (B5) CaCM-Starch respectively (yellow arrow points to the respective treatment's). All data is represented as the mean $\pm$ SD ($n = 6$). Reprinted with permission from Panwar, V., Sharma, A., Thomas, J., *et al.*, 2019. *In-vitro* and *In-vivo* evaluation of biocompatible and biodegradable calcium-modified carboxymethyl starch as a topical hemostat. *Materialia* 7, 100373.

Nano-biocomposites of GG and TiO_2 nanotubes, NTs, were prepared as wound dressing materials which were satisfactorily biocompatible towards the 3T3 mouse fibroblast cells and exhibited favorable wound healing activities to the open excision wounds created on Sprague Dawley rats (Fig. 16; Razali *et al.*, 2020). Also, the nanocomposite containing 20 w/w% of TiO_2 nanotubes displayed the utmost antibacterial capacity against *Pseudomonas aeruginosa*, *Escherichia coli*, *Streptococcus* and *Staphylococcus aureus* bacteria with inhibition zones were 12 ± 0.25 , 14 ± 0.06 , 16 ± 0.06 and 16 ± 0.06 mm, respectively. Composites of GG and Manuka honey were achieved indicating inherent antibacterial characteristics against *S. epidermidis* and *S. aureus* clinical microorganisms, and greater mechanical properties compared to those of the natural hydrogels such as CS, alginate and HA (Bonifacio *et al.*, 2018). Additionally, they did not reveal cytotoxicity to the human mesenchymal stem cells and displayed constant collagen II expression and large synthesis of proteoglycans and glycosaminoglycans according to the chondrogenesis tests approving the cartilage matrix formation. Hence, such smart biocomposites were considered as promising biomaterials for the cartilage tissue engineering. Some composite were developed based on GG, guar gum and hydroxyapatite through the freeze

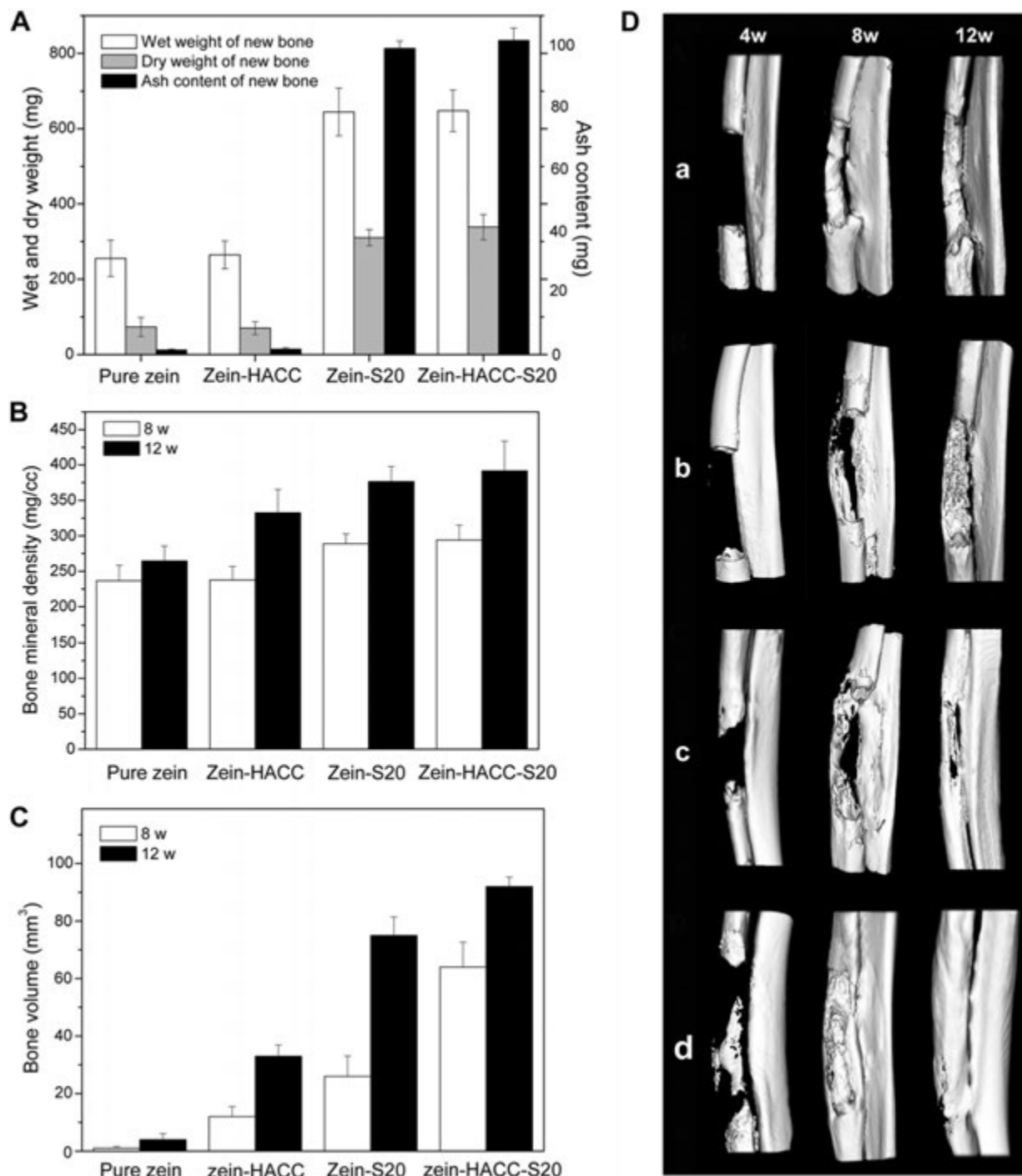


Fig. 15 (A) Wet, dry, and ash weight of ectopically formed bone induced by different composite scaffolds after 4 weeks of implantation. Note: the data on ash content is represented with the second Y-axis to the graph. (B) Quantitative analysis of mineralized new bone formation from SRmCT images: bone mineral density at 8 and 12 weeks. (C) Regenerated bone volume at both 8 and 12 weeks. (D) 3D Micro-CT reconstructed images of rabbit segmental radius at 4, 8, and 12 weeks with different implants: (a) pure zein scaffold, (b) zein-HACC, (c) zein-S20, and (d) zein-HACC-S20 scaffolds. Reprinted with permission from Zhou, P., Xia, Y., Cheng, X., *et al.*, 2014. Enhanced bone tissue regeneration by antibacterial and osteoinductive silica-HACC-zein composite scaffolds loaded with rhBMP-2. *Biomaterials* 35 (38), 10033–10045.

drying technique that were applied in bone tissue engineering (Anandan *et al.*, 2019). The optimized scaffold displayed a minimum swelling and only 13.7% degradation in the phosphate buffered saline medium during 21 days. Furthermore, it did not show any cytotoxicity to the MG63 osteosarcoma and L929 murine fibroblast cells because the cells were well proliferated on the scaffold as established using the MTT assay for 1, 4 and 7 days. Nanocomposite films of GG and TiO₂ nanoparticles were achieved

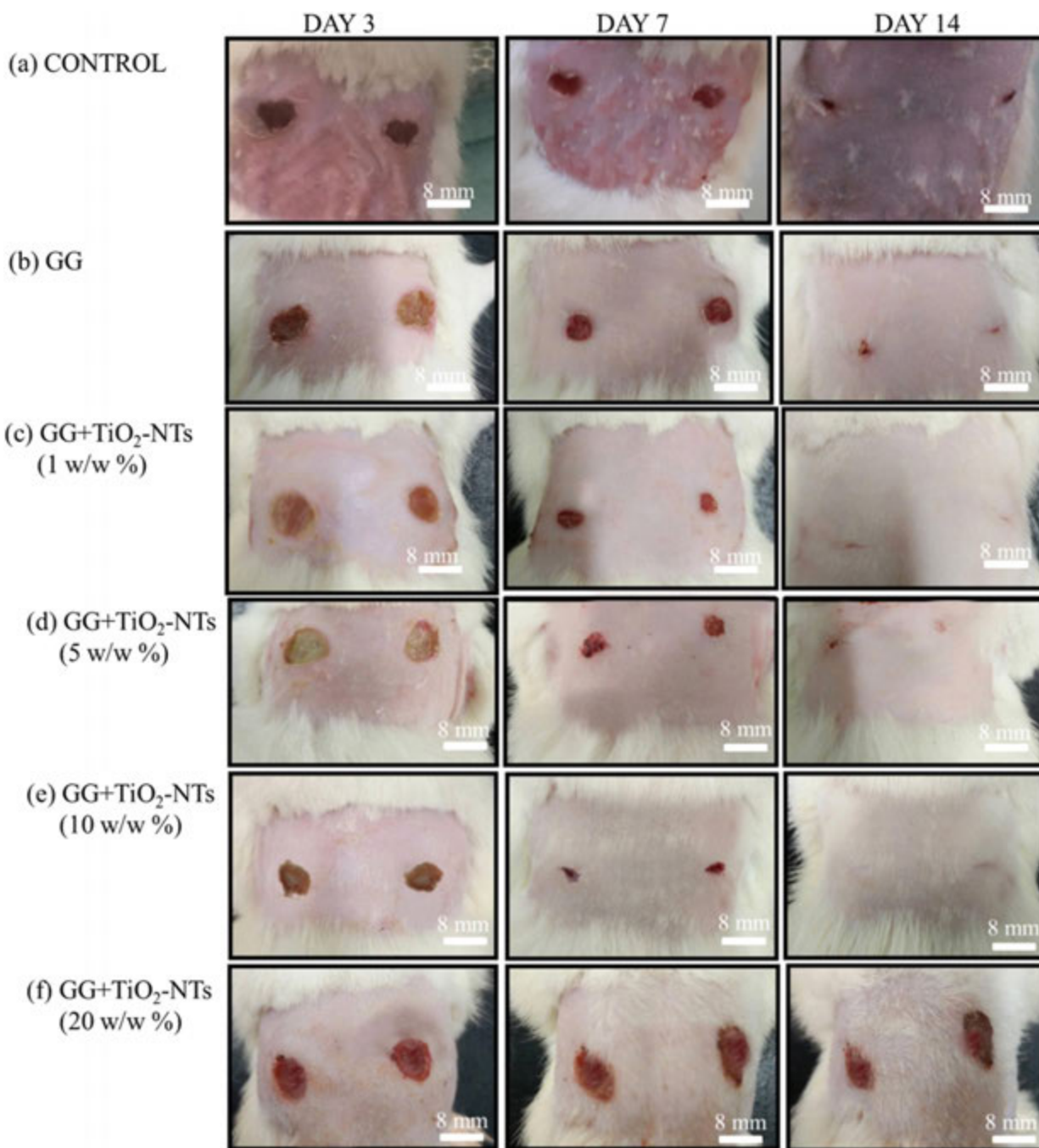


Fig. 16 Macroscopic photographs of the wounds treated using (a) Control, (b) GG, (c) GG + TiO₂ NTs (1 w/w%), (d) GG + TiO₂ NTs (5 w/w%), (e) GG + TiO₂ NTs (10 w/w%), and (f) GG + TiO₂ NTs (20 w/w%) films. Reprinted with permission from Razali, M.H., Ismail, N.A., Mat Amin, K.A., 2020. Titanium dioxide nanotubes incorporated gellan gum bio-nanocomposite film for wound healing: effect of TiO₂ nanotubes concentration. *International Journal of Biological Macromolecules* 153, 1117–1135.

as effective wound dressings which illustrated suitable antibacterial activities with 11 ± 0.06 and 9 ± 0.25 mm growth inhibition zones against *E. coli* and *S. aureus* bacteria, respectively (Bonifacio *et al.*, 2020). Moreover, the GG/TiO₂ nano-biofilm was not cytotoxic to mouse fibroblast cells as it revealed superior migration and proliferation of the cells and accelerated healing of open excision wounds created on Sprague Dawley rats in 14 days but the GG-treated wounds did not completely healed. Biocomposites of GG and high-methoxyl pectin modified with diethanolamine encapsulated the olive oil and used in intra-gastric controlled delivery of metformin HCl so that different drug encapsulation efficiency of 50%–85% and prolonged drug release activities of 69%–94% were measured in acetate buffer with pH = 4.5 (Bera *et al.*, 2018). Three-dimensionally bioprinted high fidelity human scale nose and ear tissues were constructed using GG (with greater shear thinning and recovery) and poly(ethylene glycol)

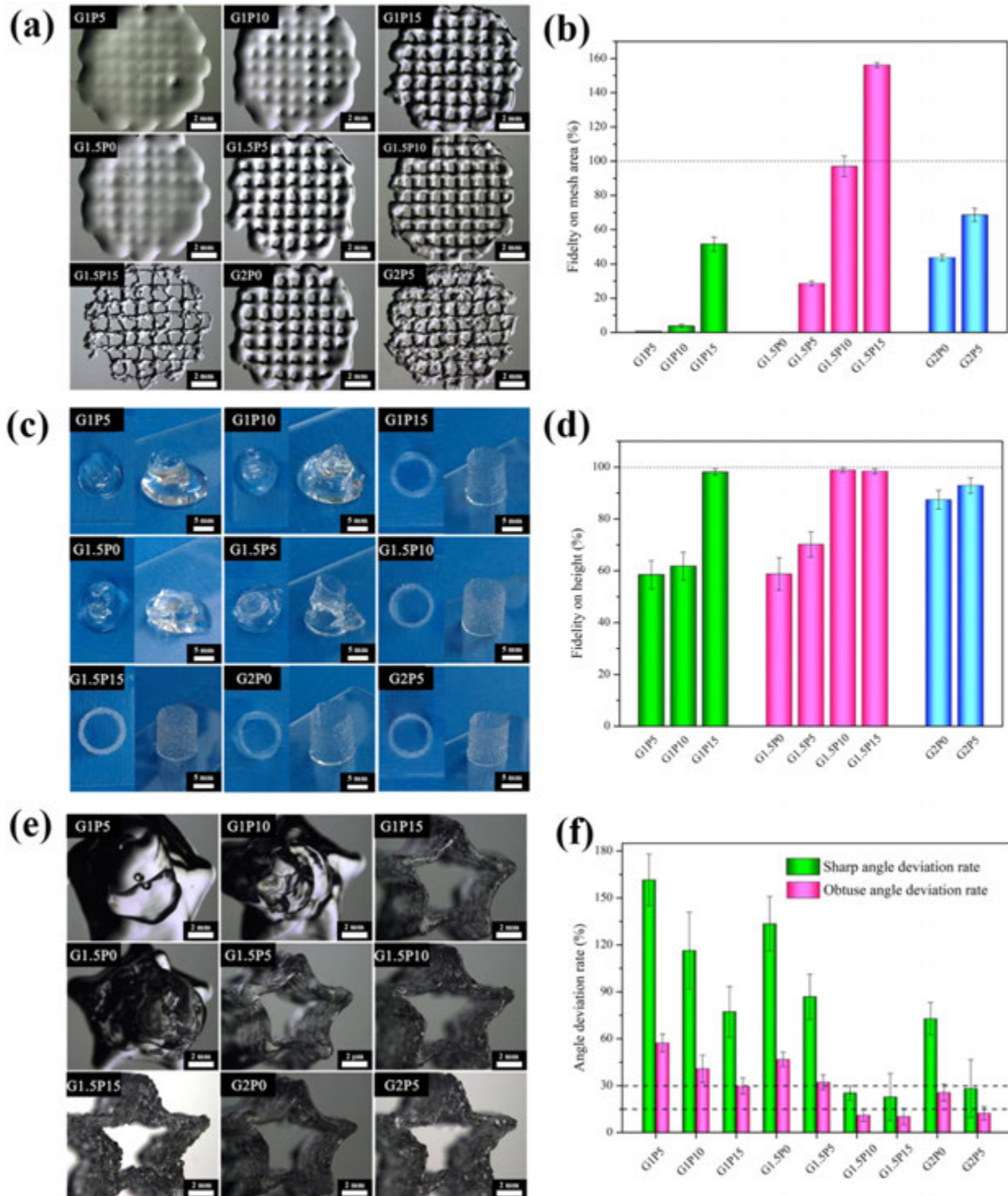


Fig. 17 Printability of GG/PEGDA hydrogels. (a, c, e) Optical images of printed 3D structures. (b, d, f) The printing fidelity for the bioink candidates. Reprinted with permission from Wu, D., Yu, Y., Tan, J., *et al.*, 2018. 3D bioprinting of gellan gum and poly (ethylene glycol) diacrylate based hydrogels to produce human-scale constructs with high-fidelity. *Materials & Design* 160, 486–495.

diacrylate (with fast UV crosslinking ability) by extrusion method, see Figs. 17 and 18 (Wu *et al.*, 2018). Murine bone marrow stromal cells and MC3T3-E1 mouse osteoblastic cells were encapsulated into the hydrogels and extraordinary cell viability percentages of >87% were achieved during 21 days.

Biocomposite of GA and hollow silica spheres modified by the epoxidation reaction using epichlorohydrin was fabricated as a non-cytotoxic material and loaded by methylene blue which exhibited wound healing effect as 55% wound closure was observed

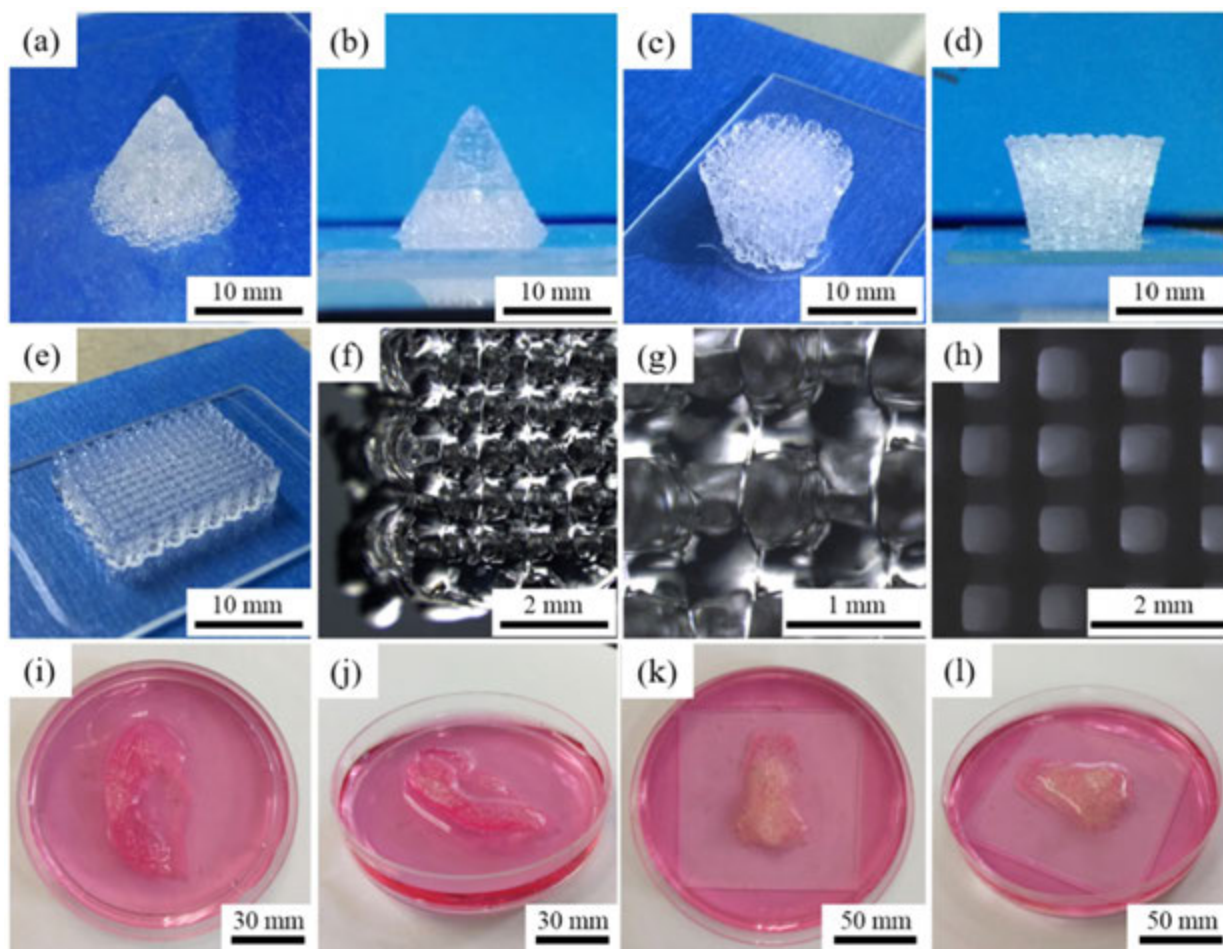


Fig. 18 The images of several 3D printed models by Ink G1.5P10. Aerial view (a) and left view (b) images of a sharp cone structure. Aerial view (c) and left view (d) images of a reverse square prism structure. (e) The aerial view images of a cuboid structure. Its partial enlarged images by stereoscope are also shown as (f), (g), (h) (after treated with liquid nitrogen). Top view (i) and aerial view (j) images of a 3D printed hydrogel human ear. Top view (k) and aerial view (l) images of a 3D printed hydrogel human nose. Reprinted with permission from Wu, D., Yu, Y., Tan, J., *et al.*, 2018. 3D bioprinting of gellan gum and poly (ethylene glycol) diacrylate based hydrogels to produce human-scale constructs with high-fidelity. *Materials & Design* 160, 486–495.

using 100 µg/mL of the composite (Duran *et al.*, 2019). GA was attached to the alginate through covalent bonds and the prepared hydrogen was incorporated with ZnO nanoparticles (Manuja *et al.*, 2020). The nanocomposite was topically used on full-thickness excision wounds in rabbits that revealed wound healing accelerated.

Nanocomposite hydrogels were obtained as wound dressings based on GUG conjugated polyacrylamidoglycolic acid, AgNO₃ and NaBH₄ which were injectable, self-healing and antibacterial materials (Palem *et al.*, 2019). An antibacterial nanocomposite was fabricated using poly(methyl methacrylate) grafted GUG and Zn, Ce substituted hydroxyapatite for application in orthopedics (Priya *et al.*, 2018). It was illustrated that the nanocomposite led to integration/adhesion of human osteoblast cells, augmented development/proliferation of fresh bone and declined the possibility of cartilage structure collapse.

Chronotherapeutic carriers were prepared and loaded by the propranolol HCl drug using several biopolymers like TG, CS and Okra gum for targeted colon drug delivery and treatment of blood pressure at early morning (Newton *et al.*, 2015). The *in vitro* drug release tests were done within 0.1 N HCl for 1.5 h, then in phosphate buffer (pH 6.8) for 2 h and finally in phosphate buffer (pH 7.4) to measure the highest drug release amount. It was found that the formulation fabricated by the TG could prolong the drug release for longer times among other formulations. Several muco-adhesive tea tablets that were orally disintegrated and used in oral care purposes were developed through microwave radiation containing 1 w/w% of TG, GA, GUG, carrageenan or PEC or polysaccharides which exhibited antibacterial activities against *Streptococcus mutans* bacterium (Kiniwa *et al.*, 2019).

Antimicrobial and magnetic patches were achieved using XG, bovine serum albumin, Fe₃O₄ nanoparticles and amoxicillin drug to release the drug through magnetic stimulation (Bueno *et al.*, 2018). The patch contained 0.2 wt% of Fe₃O₄ released *in vitro* the drug at pH 5.5 and 0.02 mol/L of NaCl solution when exposed to the electromagnetic field followed by quasi-Fickian diffusion. The diffusion of drug molecules from patches into the agar including *E. coli* and *S. aureus* bacteria inhibited the bacterial growth. Also, the *E. coli* growth inhibition was especially effective when electromagnetic field was applied. Composite microspheres of XG

and CaCO_3 were fabricated by a mineralization biomimetic technique and used in adsorption of the lysozyme protein (Xu *et al.*, 2018). The microspheres efficiently immobilized the lysozyme through electrostatic attractions adsorption quantity and rate were $18.7 \pm 1.2 \mu\text{g}/\text{mg}$ and $58.55 \pm 0.56\%$, respectively at pH 7.0 but they were $24.3 \pm 0.1 \mu\text{g}/\text{mg}$ and $80.97 \pm 0.15\%$ at pH 9.0.

Medical Applications of Pectin, Collagen and Polyhydroxy Butyrate Composites

The pectin (PEC), collagen (COL) and polyhydroxy butyrate (PHB) composites are valuable biomaterials which are frequently employed in various medical purposes. Herein, several instances are presented to show the importance of such substances.

A porous composite was developed based on PEC, GEL and biphasic calcium phosphate loaded with vascular endothelial growth factor and bone morphogenetic protein-2 (VEGF and BMP-2) to transport growth factors to bones for bone formation/regeneration/healing (Amirian *et al.*, 2015). The scaffolds incorporated with the VEGF and BMP-2 increased the spreading, proliferation and viability of MC3T3-E1 preosteoblasts were investigated relative to the scaffolds prepared without these growth factors. Also, bone formation *in vivo* in rats was happened using the composites containing VEGF and BMP-2 in four weeks which was greater in the BMP-2 loaded scaffold. Magnetic thermo- and pH- dual responsive microgels were prepared using PEC maleate, Fe_3O_4 nanoparticles and N-isopropyl acrylamide that were encapsulated with curcumin drug and used as drug vehicles (Almeida *et al.*, 2017). The curcumin release was sustainable and slow by applying an external magnetic field. Composite films of quaternized PEC and montmorillonite mineral were obtained and loaded with 5-fluorouracil anticancer drug as drug delivery formulations (Meng *et al.*, 2020).

A composite of COL and octacalcium phosphate was fabricated as an implant to induce the bone regeneration in bone defects of rodent, canine and human (Kanda *et al.*, 2016). It was found that the implantation inside the alveolar area including the unerupted permanent successor teeth was disturbed the permanent tooth eruption but preserved the alveolar ridge (Figs. 19 and 20). Magnetic COL nano-biocomposite was developed as the MRI contrast agent and as a targeted carrier for application in cancer treatment (Mandal *et al.*, 2013). The COL nanofibers were fabricated using Fe_3O_4 nanoparticles, fluorescein isothiocyanate labeled antibody and gemcitabine anticancer drug. This NBC was characterized by conventional methods and evaluated for its biological activities. The MRI scan indicated a superparamagnetic property for the COL nanocomposite confirming it was a good MRI contrast agent. The MTT test approved that the COL nanobiocomposite was biocompatible towards the Hep2 Human epithelial type 2 cells but it exhibited an apoptotic influence by the receptor assisted endocytosis and cellular uptake.

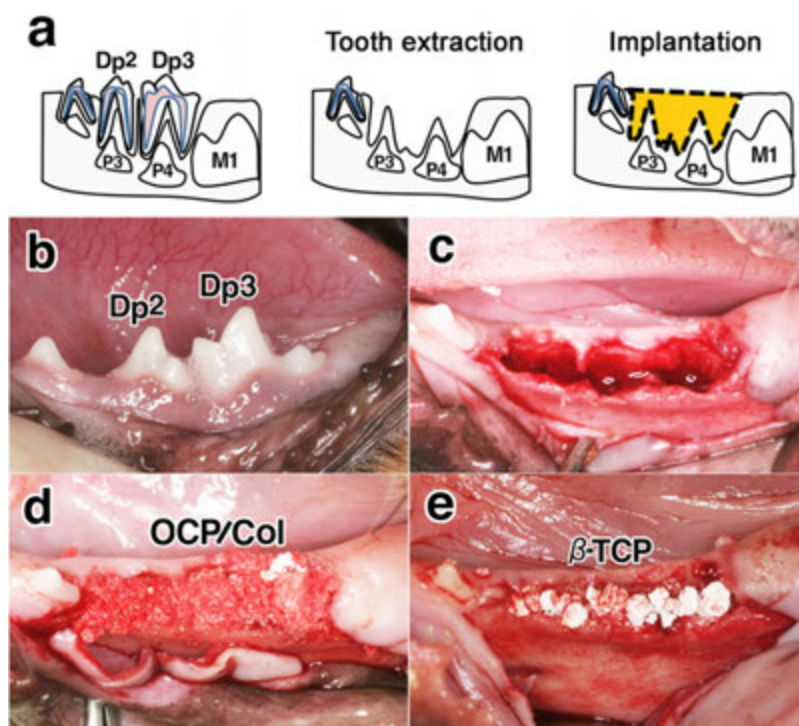


Fig. 19 (a) Implantation processes, (b) before tooth extraction, (c) preparation of implant beds after removing the alveolar septum of the Dp2 and Dp3 (untreated group), (d) implantation of OCP/Col (OCP/Col group), (e) implantation of β -TCP (β -TCP group); Dp2: second deciduous premolar, Dp3: third deciduous premolar, P3: third premolar, P4: fourth premolar, M1: first molar. Reprinted with permission from Kanda, N., Matsui, K., Kawai, T., *et al.*, 2016. Implantation of octacalcium phosphate collagen composites (OCP/Col) after extraction of canine deciduous teeth achieved undisturbed permanent tooth eruption. Archives of Oral Biology 72, 179–186.

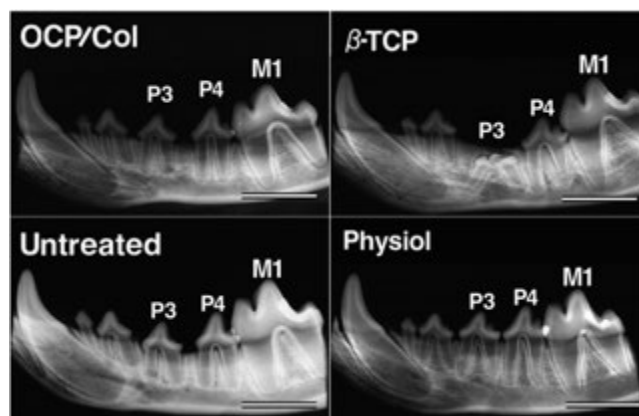


Fig. 20 Radiographic images indicating the OCP/Col tends to have eruptive positions of the third and fourth premolars (P3 and P4) and alveolar heights which are comparable to those of Physiol. The β -TCP and untreated groups tend to have lower eruptive positions of the third and fourth premolars and alveolar heights. Bars: 20 mm. Reprinted with permission from Kanda, N., Matsui, K., Kawai, T., *et al.*, 2016. Implantation of octacalcium phosphate collagen composites (OCP/Col) after extraction of canine deciduous teeth achieved undisturbed permanent tooth eruption. *Archives of Oral Biology* 72, 179–186.

Composite scaffolds of PHB-co-hydroxyvalerate copolymer conjugated graphite oxide and Fe_3O_4 nanoparticles were synthesized that were thermally and mechanically stable and employed in tissue engineering and bio-imaging by acquisition of phantom agar MRI images due to the existence of the Fe_3O_4 nanoparticles used as a negative T2 contrast material with greater relaxivity (Pramanik *et al.*, 2019). The Composite scaffolds exhibited higher antibacterial properties against Gram-negative strains (*E. coli* and *P. aeruginosa*) than Gram-positive bacteria (*B. subtilis* and *S. aureus*). Noteworthy adhesion as well as 85% proliferation of NIH 3T3 fibroblast cells were observed onto the nanocomposite surface indicating its biocompatibility and physiological stability. Bionanocomposites of PHB and Co_3O_4 were fabricated which illustrated the highest bactericidal activities against *S. aureus* and *E. coli* as multidrug resistant microbes (Safaei *et al.*, 2020). Porous composites of PHB and hydroxyapatite (HAP) were fabricated containing various amounts of HAP including 10, 20, 30, 40, 50 wt% (Senatov *et al.*, 2017). The PHB-20%HAP and PHB composites were *in vitro* adhered onto the mouse multipotent mesenchymal stromal cells so that the PHB-20% HAP more effectively induced proliferation of cells ($31 \pm 6.1\%$) than PHB ($20 \pm 5.7\%$). The PHB-20%HAP composite was resorbed (indicating 49% decrease in the implant surface area) and integrated to the neighboring tissues 30 days post implantation. Also, accumulation of osteoclasts, angiogenesis and formation of fresh bone proved that the PHB-20%HAP was a favorable material in bone tissue engineering. The PHB polymer was isolated from *Bacillus cereus* strain VIT-SSR1 using a contaminated industrial waste and the PHB/CS blended films encapsulated with the curcumin drug were fabricated which indicated a sustained drug release and their biocompatibility were examined by the MTT test using L929 mouse fibroblast cells (Evangeline and Sridharan, 2019).

Conclusion

Natural biopolymers and their composites can replace the synthetic polymers as the fossil fuel based polymers reveal numerous side effects. It has been recognized that the synthetic petroleum derived polymers have many unfavorable environmental issues. Also, they are usually left at landfills, soils and oceans without degradation leading to the environmental pollution. Therefore, biodegradable polymers can be used to solve these contaminations. Moreover, biopolymers and their composites are increasingly employed in therapeutic and surgical applications, tissue regeneration, biomedicine, drug carriers, radiotherapy, imaging and diagnosis, temporary prostheses, adhesion/fixation/suturing biomaterials and implants. The biopolymers marketplace grows quickly by enhancement in the social attention to the sustainable environment. Although utilization of synthetic polymers (and plastics) instead of the biopolymers is an important subject, the production of biopolymers in large scales still is not cost effective. Thus, it is necessary to perform more extensive investigations to find economical methods for the synthesis or fabrication of biopolymers and their composites from biomasses.

Biological polymers and their composites exhibit several benefits compared to the extensively utilized synthetic polymers because they are biocompatible, bioactive, biodegradable, renewable, environmentally benign and may reveal antibacterial/anti-inflammation capacities. For instance, biopolymer composite scaffolds have been used in clinical trials to repair the bone, skin, cartilage, human organs and vascular grafts, completely bio-barrier membranes and absorbable stents without needing subsequent surgery. Moreover, biopolymer composites are developed as systems releasing bioactive agents and drugs as multifunctional formulations preserving the properties of all encapsulated biomolecules.

Most biopolymers illustrate poor mechanical features relative to those of the synthetic polymers. Thus, different procedures are adopted to improve their mechanical properties including adding nano/micro-particles as fillers, plasticizers, and conjugating biopolymers and/or biopolymer blends. Natural biopolymers are mostly incorporated with bioactive substances, nano/micro-materials and/or other polymers

in order to achieve matrixes well mimicking the ECM. Numerous biopolymers are commonly commercially employed by researchers and industries such as chitosan, carboxymethyl chitosan, alginate, hyaluronic acid, cellulose, carboxymethyl cellulose, starch, carboxymethyl starch, gellan gum, gum acacia/gum arabic, guar gum, tamarind gum, xanthan gum, gelatin, zein, chondroitin sulfate, polyhydroxy butyrate, pectin and collagen. It has been frequently shown that incorporation of inorganic nano-/micro-materials as fillers improves the physical and structural characteristics of biopolymers such as their moisture sensitivity, gas permeability, mechanical strength, shelf life, antifungal and antibacterial activities. The biopolymer composites are extensively utilized in different biomedical applications such as surgical implants, drug delivery formulations, vaccines, tissue engineering, imaging and diagnosis though they have found numerous other applications including smart materials, packaging, electronics, food products, construction, biosensors, conductive and antibacterial papers and textiles.

Acknowledgments

The financial support of this work by Research Office of Amirkabir University of Technology (Tehran Polytechnic) is gratefully acknowledged.

References

- Almeida, E.A.M.S., Bellettini, I.C., Garcia, F.P., *et al.*, 2017. Curcumin-loaded dual pH- and thermo-responsive magnetic microcarriers based on pectin maleate for drug delivery. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 171. Elsevier, pp. 259–266.
- Amirian, J., Linh, N.T.B., Min, Y.K., Lee, B.-T., 2015. Bone formation of a porous Gelatin-Pectin-biphasic calcium phosphate composite in presence of BMP-2 and VEGF. *International Journal of Biological Macromolecules* 76, 10–24.
- Anandan, D., Madhumathi, G., Nambiraj, N.A., Jaiswal, A.K., 2019. Gum based 3D composite scaffolds for bone tissue engineering applications. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 214. Elsevier, pp. 62–70.
- Andreasen, C.M., Henriksen, S.S., Ding, M., *et al.*, 2017. The efficacy of poly-D,L-lactic acid- and hyaluronic acid-coated bone substitutes on implant fixation in sheep. *Journal of Orthopaedic Translation* 8, 12–19.
- Ashe, S., Behera, S., Dash, P., Nayak, D., Nayak, B., 2020. Gelatin carrageenan sericin hydrogel composites improves cell viability of cryopreserved SaOS-2 cells. *International Journal of Biological Macromolecules* 154, 606–620.
- Barros, J.A.R., de Melo, L.D.R., da Silva, R.A. R., *et al.*, 2020. Encapsulated bacteriophages in alginate-nanohydroxyapatite hydrogel as a novel delivery system to prevent orthopedic implant-associated infections. *Nanomedicine: Nanotechnology, Biology and Medicine* 24, 102145.
- Bera, H., Kumar, S., Maiti, S., 2018. Facile synthesis and characterization of tailor-made pectin-gellan gum-bionanofiller composites as intragastric drug delivery shuttles. *International Journal of Biological Macromolecules* 118, 149–159.
- Biranje, S.S., Madiwale, P.V., Patankar, K.C., *et al.*, 2020. Cytotoxicity and hemostatic activity of chitosan/carrageenan composite wound healing dressing for traumatic hemorrhage. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 239. Elsevier, 116106.
- Bonifacio, M.A., Cometa, S., Cochis, A., *et al.*, 2018. Antibacterial effectiveness meets improved mechanical properties: Manuka honey/gellan gum composite hydrogels for cartilage repair. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 198. Elsevier, pp. 462–472.
- Bonifacio, M.A., Cochis, A., Cometa, S., *et al.*, 2020. Advances in cartilage repair: The influence of inorganic clays to improve mechanical and healing properties of antibacterial Gellan gum-Manuka honey hydrogels. *Materials Science and Engineering: C* 108, 110444.
- Bueno, P.V.A., Hilamatu, K.C.P., Carmona-Ribeiro, A.M., Petri, D.F.S., 2018. Magnetically triggered release of amoxicillin from xanthan/Fe3O4/albumin patches. *International Journal of Biological Macromolecules* 115, 792–800.
- Cai, X., Hu, S., Yu, B., *et al.*, 2018. Transglutaminase-catalyzed preparation of crosslinked carboxymethyl chitosan/carboxymethyl cellulose/collagen composite membrane for postsurgical peritoneal adhesion prevention. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 201. Elsevier, pp. 201–210.
- Chen, S., Han, Y., Sun, C., *et al.*, 2018. Effect of molecular weight of hyaluronan on zein-based nanoparticles: Fabrication, structural characterization and delivery of curcumin. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 201. Elsevier, pp. 599–607.
- Chen, Y., Qiu, H., Dong, M., *et al.*, 2019. Preparation of hydroxylated lecithin complexed iodine/carboxymethyl chitosan/sodium alginate composite membrane by microwave drying and its applications in infected burn wound treatment. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 206. Elsevier, pp. 435–445.
- Cheng, F., Wu, Y., Li, H., *et al.*, 2019. Biodegradable N, O-carboxymethyl chitosan/oxidized regenerated cellulose composite gauze as a barrier for preventing postoperative adhesion. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 207. Elsevier, pp. 180–190.
- Dashdorj, U., Reyes, M.K., Unnithan, A.R., *et al.*, 2015. Fabrication and characterization of electrospun zein/Ag nanocomposite mats for wound dressing applications. *International Journal of Biological Macromolecules* 80, 1–7.
- Duran, H., Üstün Alkan, F., Ulkay, M.B., *et al.*, 2019. Investigation of the *in vitro* cytotoxic effects and wound healing activity of ternary composite substance (hollow silica sphere/gum arabic/methylene blue). *International Journal of Biological Macromolecules* 121, 1194–1202.
- Evangelina, S., Sridharan, T.B., 2019. Biosynthesis and statistical optimization of polyhydroxyalkanoate (PHA) produced by *Bacillus cereus* VIT-SSR1 and fabrication of biopolymer films for sustained drug release. *International Journal of Biological Macromolecules* 135, 945–958.
- Fazli, Y., Shariatnia, Z., 2017. Controlled release of cefazolin sodium antibiotic drug from electrospun chitosan-polyethylene oxide nanofibrous mats. *Materials Science and Engineering C* 71, 641–652.
- Fazli, Y., Shariatnia, Z., Kohsari, I., Azadmehr, A., Pourmortazavi, S.M., 2016. A novel chitosan-polyethylene oxide nanofibrous mat designed for controlled co-release of hydrocortisone and imipenem/cilastatin drugs. *International Journal of Pharmaceutics* 513 (1–2), 636–647.
- Fenbo, M., Xingyu, X., Bin, T., 2019. Strontium chondroitin sulfate/silk fibroin blend membrane containing microporous structure modulates macrophage responses for guided bone regeneration. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 213. Elsevier, pp. 266–275.
- George, A., Sanjay, M.R., Srisuk, R., Parameswaranpillai, J., Siengchin, S., 2020. A comprehensive review on chemical properties and applications of biopolymers and their composites. *International Journal of Biological Macromolecules* 154, 329–338.
- Gordon-Wylie, S.W., Solamen, L.M., McGarry, M.D.J., *et al.*, 2018. MR elastography at 1 Hz of gelatin phantoms using 3D or 4D acquisition. *Journal of Magnetic Resonance* 296, 112–120.
- Hafezi Moghaddam, R., Dadfarnia, S., Shabani, A.M.H., Amraei, R., Hafezi Moghaddam, Z., 2020. Doxycycline drug delivery using hydrogels of O-carboxymethyl chitosan conjugated with caffeic acid and its composite with polyacrylamide synthesized by electron beam irradiation. *International Journal of Biological Macromolecules* 154, 962–973.

- Hemalatha, T., Prabu, P., Gunadharini, D.N., Gowthaman, M.K., 2018. Fabrication and characterization of dual acting oleyl chitosan functionalised iron oxide/gold hybrid nanoparticles for MRI and CT imaging. *International Journal of Biological Macromolecules* 112, 250–257.
- Jahanban-Estahlan, R., Derakhshankhah, H., Haghshenas, B., *et al.*, 2020. A bio-inspired magnetic natural hydrogel containing gelatin and alginate as a drug delivery system for cancer chemotherapy. *International Journal of Biological Macromolecules* 156, 438–445.
- Kabir, E., Kaur, R., Lee, J., Kim, K.-H., Kwon, E.E., 2020. Prospects of biopolymer technology as an alternative option for non-degradable plastics and sustainable management of plastic wastes. *Journal of Cleaner Production* 258, 120536.
- Kanda, N., Matsui, K., Kawai, T., *et al.*, 2016. Implantation of octacalcium phosphate collagen composites (OCP/Col) after extraction of canine deciduous teeth achieved undisturbed permanent tooth eruption. *Archives of Oral Biology* 72, 179–186.
- Kassem, A., Ayoub, G.M., Malaeb, L., 2019. Antibacterial activity of chitosan nano-composites and carbon nanotubes: a review. *Science of The Total Environment* 668, 566–576.
- Kazemi, S., Daryani, A.S., Abdouss, M., Shariatnia, Z., 2016. DFT computations on the hydrogen bonding interactions between methacrylic acid-trimethylolpropane trimethacrylate copolymers and letrozole as drug delivery systems. *Journal of Theoretical and Computational Chemistry* 15 (02), 1650015.
- Khan, M.A., Mujahid, M., 2019. A review on recent advances in chitosan based composite for hemostatic dressings. *International Journal of Biological Macromolecules* 124, 138–147.
- Kim, H.S., Sun, X., Lee, J.-H., *et al.*, 2019. Advanced drug delivery systems and artificial skin grafts for skin wound healing. *Advanced Drug Delivery Reviews* 146, 209–239.
- Kim, Y.-K., Kim, S.-Y., Jang, Y.-S., Park, I.-S., Lee, M.-H., 2020. Bio-corrosion behaviors of hyaluronic acid and cerium multi-layer films on degradable implant. *Applied Surface Science* 515, 146070.
- Kiniwa, R., Miyake, M., Kimura, S.-i., *et al.*, 2019. Development of muco-adhesive orally disintegrating tablets containing tamarind gum-coated tea powders for oral care. *International Journal of Pharmaceutics* X 1, 100012.
- Kohsari, I., Shariatnia, Z., Pourmortazavi, S.M., 2016a. Antibacterial electrospun chitosan-polyethylene oxide nanocomposite mats containing ZIF-8 nanoparticles. *International Journal of Biological Macromolecules* 91, 778–788.
- Kohsari, I., Shariatnia, Z., Pourmortazavi, S.M., 2016b. Antibacterial electrospun chitosan-polyethylene oxide nanocomposite mats containing bioactive silver nanoparticles. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 140. Elsevier, pp. 287–298.
- Cacicedo, M.L., E. León, I., Gonzalez, J.S., *et al.*, 2016. Modified bacterial cellulose scaffolds for localized doxorubicin release in human colorectal HT-29 cells. *Colloids and Surfaces B: Biointerfaces* 140, 421–429.
- Lai, Y.-L., Cheng, Y.-M., Yen, S.-K., 2019. Doxorubicin - chitosan - hydroxyapatite composite coatings on titanium alloy for localized cancer therapy. *Materials Science and Engineering C* 104, 109953.
- Lee, J.-Y., Park, J.-H., Lee, J.-J., *et al.*, 2016. Polyethylene glycol-conjugated chondroitin sulfate A derivative nanoparticles for tumor-targeted delivery of anticancer drugs. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 151. Elsevier, pp. 68–77.
- Leonida, M., Ispas-Szabo, P., Mateescu, M.A., 2018. Self-stabilized chitosan and its complexes with carboxymethyl starch as excipients in drug delivery. *Bioactive Materials* 3 (3), 334–340.
- Li, T., Song, X., Weng, C., *et al.*, 2018. Self-crosslinking and injectable chondroitin sulfate/pullulan hydrogel for cartilage tissue engineering. *Applied Materials Today* 10, 173–183.
- Lin, C., Sun, K., Zhang, C., *et al.*, 2020. Carbon dots embedded metal organic framework @ chitosan core-shell nanoparticles for vitro dual mode imaging and pH-responsive drug delivery. *Microporous and Mesoporous Materials* 293, 109775.
- Ling, S., Chen, W., Fan, Y., *et al.*, 2018. Biopolymer nanofibrils: structure, modeling, preparation, and applications. *Progress in Polymer Science* 85, 1–56.
- Liu, F., Li, X., Wang, L., *et al.*, 2020. Sesamol incorporated cellulose acetate-zein composite nanofiber membrane: an efficient strategy to accelerate diabetic wound healing. *International Journal of Biological Macromolecules* 149, 627–638.
- Liu, K., Wang, Y., Li, H., Duan, Y., 2015. A facile one-pot synthesis of starch functionalized graphene as nano-carrier for pH sensitive and starch-mediated drug delivery. *Colloids and Surfaces B: Biointerfaces* 128, 86–93.
- Liu, P., Shen, H., Zhi, Y., *et al.*, 2019. 3D bioprinting and *in vitro* study of bilayered membranous construct with human cells-laden alginate/gelatin composite hydrogels. *Colloids and Surfaces B: Biointerfaces* 181, 1026–1034.
- Malik, M.H., Shahzadi, L., Batool, R., *et al.*, 2020. Thyroxine-loaded chitosan/carboxymethyl cellulose/hydroxyapatite hydrogels enhance angiogenesis in in-ovo experiments. *International Journal of Biological Macromolecules* 145, 1162–1170.
- Mandal, A., Sekar, S., Kanagavel, M., *et al.*, 2013. Collagen based magnetic nanobiocomposite as MRI contrast agent and for targeted delivery in cancer therapy. *Biochimica et Biophysica Acta (BBA) - General Subjects* 1830 (10), 4628–4633.
- Manuja, A., Raguvanan, R., Kumar, B., Kalra, A., Tripathi, B.N., 2020. Accelerated healing of full thickness excised skin wound in rabbits using single application of alginate/ acacia based nanocomposites of ZnO nanoparticles. *International Journal of Biological Macromolecules* 155, 823–833.
- Matinfar, M., Mesgar, A.S., Mohammadi, Z., 2019. Evaluation of physicochemical, mechanical and biological properties of chitosan/carboxymethyl cellulose reinforced with multiphasic calcium phosphate whisker-like fibers for bone tissue engineering. *Materials Science and Engineering C* 100, 341–353.
- Mauricio, M.R., da Costa, P.G., Haraguchi, S.K., *et al.*, 2015. Synthesis of a microhydrogel composite from cellulose nanowhiskers and starch for drug delivery. In: Kennedy, J. F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 115. Elsevier, pp. 715–722.
- Mazloom-Jalali, A., Shariatnia, Z., 2019. Polycaprolactone nanocomposite systems used to deliver ifosfamide anticancer drug: Molecular dynamics simulations. *Structural Chemistry* 30 (3), 863–876.
- Mazloom-Jalali, A., Shariatnia, Z., Tamai, I.A., Pakzad, S.-R., Malakootikhah, J., 2020. Fabrication of chitosan-polyethylene glycol nanocomposite films containing ZIF-8 nanoparticles for application as wound dressing materials. *International Journal of Biological Macromolecules* 153, 421–432.
- Meng, Y.-j., Wang, S.-y., Guo, Z.-w., *et al.*, 2020. Design and preparation of quaternized pectin-Montmorillonite hybrid film for sustained drug release. *International Journal of Biological Macromolecules* 154, 413–420.
- Min, T., Zhu, Z., Sun, X., *et al.*, 2020. Highly efficient antifogging and antibacterial food packaging film fabricated by novel quaternary ammonium chitosan composite. *Food Chemistry* 308, 125682.
- Mohapatra, S., Asfer, M., Anwar, M., *et al.*, 2018. Carboxymethyl Assam Bora rice starch coated SPIONs: Synthesis, characterization and *in vitro* localization in a micro capillary for simulating a targeted drug delivery system. *International Journal of Biological Macromolecules* 115, 920–932.
- Negm, N.A., Hefni, H.H.H., Abd-Elal, A.A.A., Badr, E.A., Abou Kana, M.T.H., 2020. Advancement on modification of chitosan biopolymer and its potential applications. *International Journal of Biological Macromolecules* 152, 681–702.
- Newton, A.M.J., Indana, V.L., Kumar, J., 2015. Chronotherapeutic drug delivery of tamarind gum, chitosan and okra gum controlled release colon targeted directly compressed propranolol HCl matrix tablets and *in-vitro* evaluation. *International Journal of Biological Macromolecules* 79, 290–299.
- Nikfar, Z., Shariatnia, Z., 2017a. DFT computational study on the phosphate functionalized SWCNTs as efficient drug delivery systems for anti-osteoporosis zoledronate and risedronate drugs. *Physica E: Low-Dimensional Systems and Nanostructures* 91, 41–59.
- Nikfar, Z., Shariatnia, Z., 2017b. Phosphate functionalized (4, 4)-armchair CNTs as novel drug delivery systems for alendronate and etidronate anti-osteoporosis drugs. *Journal of Molecular Graphics and Modelling* 76, 86–105.
- Nikfar, Z., Shariatnia, Z., 2019. The RGD tripeptide anticancer drug carrier: DFT computations and molecular dynamics simulations. *Journal of Molecular Liquids* 281, 565–583.

- Ong, W., Pinese, C., Chew, S.Y., 2019. Scaffold-mediated sequential drug/gene delivery to promote nerve regeneration and remyelination following traumatic nerve injuries. *Advanced Drug Delivery Reviews* 149–150, 19–48.
- Palem, R.R., Madhusudana Rao, K., Kang, T.J., 2019. Self-healable and dual-functional guar gum-grafted-polyacrylamidoglycolic acid-based hydrogels with nano-silver for wound dressings. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 223. Elsevier, 115074.
- Pankongadisak, P., Tsekoura, E., Suwanton, O., Uludağ, H., 2020. Electrospun gelatin matrices with bioactive pDNA polyplexes. *International Journal of Biological Macromolecules* 149, 296–308.
- Panwar, V., Sharma, A., Thomas, J., *et al.*, 2019. *In-vitro* and *In-vivo* evaluation of biocompatible and biodegradable calcium-modified carboxymethyl starch as a topical hemostat. *Materialia* 7, 100373.
- Park, S.-B., Lih, E., Park, K.-S., Joung, Y.K., Han, D.K., 2017. Biopolymer-based functional composites for medical applications. *Progress in Polymer Science* 68, 77–105.
- Pedram Rad, Z., Mokhtari, J., Abbasi, M., 2019. Calendula officinalis extract/PCL/Zein/Gum arabic nanofibrous bio-composite scaffolds via suspension, two-nozzle and multilayer electrospinning for skin tissue engineering. *International Journal of Biological Macromolecules* 135, 530–543.
- Pramanik, N., Bhattacharya, S., Rath, T., *et al.*, 2019. Polyhydroxybutyrate-co-hydroxyvalerate copolymer modified graphite oxide based 3D scaffold for tissue engineering application. *Materials Science and Engineering C* 94, 534–546.
- Priya, G., Vijayakumari, N., Sangeetha, R., 2018. Novel poly (methyl methacrylate) grafted guar gum/mineral substituted apatite nanocomposites for orthopedics applications: *In vitro* physicochemical and biochemical studies. *Journal of Science: Advanced Materials and Devices* 3 (3), 317–322.
- Quadrado, R.F.N., Fajardo, A.R., 2020. Microparticles based on carboxymethyl starch/chitosan polyelectrolyte complex as vehicles for drug delivery systems. *Arabian Journal of Chemistry* 13 (1), 2183–2194.
- Rai, M., Ingle, A.P., Gupta, I., Brandelli, A., 2015. Bioactivity of noble metal nanoparticles decorated with biopolymers and their application in drug delivery. *International Journal of Pharmaceutics* 496 (2), 159–172.
- Razali, M.H., Ismail, N.A., Mat Amin, K.A., 2020. Titanium dioxide nanotubes incorporated gellan gum bio-nanocomposite film for wound healing: effect of TiO₂ nanotubes concentration. *International Journal of Biological Macromolecules* 153, 1117–1135.
- Rousselle, P., Braye, F., Dayan, G., 2019. Re-epithelialization of adult skin wounds: cellular mechanisms and therapeutic strategies. *Advanced Drug Delivery Reviews* 146, 344–365.
- Saboktakin, M.R., Maharramov, A., Ramazanov, M.A., 2009. Synthesis and characterization of superparamagnetic nanoparticles coated with carboxymethyl starch (CMS) for magnetic resonance imaging technique. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 78. Elsevier, pp. 292–295.
- Safaei, M., Taran, M., Jamshidi, L., *et al.*, 2020. Optimum synthesis of polyhydroxybutyrate-Co₃O₄ bionanocomposite with the highest antibacterial activity against multidrug resistant bacteria. *International Journal of Biological Macromolecules* 158, 477–485.
- Sanad, R.A.-B., Abdel-Bar, H.M., 2017. Chitosan-hyaluronic acid composite sponge scaffold enriched with Andrographolide-loaded lipid nanoparticles for enhanced wound healing. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 173. Elsevier, pp. 441–450.
- Senatov, F., Anisimova, N., Kiselevskiy, M., *et al.*, 2017. Polyhydroxybutyrate/hydroxyapatite highly porous scaffold for small bone defects replacement in the nonload-bearing parts. *Journal of Bionic Engineering* 14 (4), 648–658.
- Shariatnia, Z., 2019a. Pharmaceutical applications of chitosan. *Advances in Colloid and Interface Science* 263, 131–194.
- Shariatnia, Z., 2019b. Pharmaceutical applications of natural polysaccharides. In *Natural Polysaccharides in Drug Delivery and Biomedical Applications*. Elsevier, pp. 15–57.
- Shariatnia, Z., Nikfar, Z., 2013. Synthesis and antibacterial activities of novel nanocomposite films of chitosan/phosphoramidate/Fe₃O₄ NPs. *International Journal of Biological Macromolecules* 60, 226–234.
- Shariatnia, Z., Shahidi, S., 2014. A DFT study on the physical adsorption of cyclophosphamide derivatives on the surface of fullerene C60 nanocage. *Journal of Molecular Graphics and Modelling* 52, 71–81.
- Shariatnia, Z., Fazli, M., 2015. Mechanical properties and antibacterial activities of novel nanobiocomposite films of chitosan and starch. *Food Hydrocolloids* 46, 112–124.
- Shariatnia, Z., Zahraee, Z., 2017. Controlled release of metformin from chitosan-based nanocomposite films containing mesoporous MCM-41 nanoparticles as novel drug delivery systems. *Journal of Colloid and Interface Science* 501, 60–76.
- Shariatnia, Z., Jalali, A.M., 2018. Chitosan-based hydrogels: Preparation, properties and applications. *International Journal of Biological Macromolecules* 115, 194–220.
- Shariatnia, Z., Mohammadi-Denyani, A., 2018. Advances in polymers for drug delivery and wound healing applications. In *Advances in Polymers for Biomedical Applications*. Nova Science Publisher.
- Shariatnia, Z., Barzegari, A., 2019. Polysaccharide hydrogel films/membranes for transdermal delivery of therapeutics. In *Polysaccharide Carriers for Drug Delivery*. Elsevier, pp. 639–684.
- Shariatnia, Z., Mazloom-Jalali, A., 2019. Chitosan nanocomposite drug delivery systems designed for the ifosfamide anticancer drug using molecular dynamics simulations. *Journal of Molecular Liquids* 273, 346–367.
- Shariatnia, Z., Fasihozaman-Langroodi, K., 2019. Biodegradable Polymer Nanobiocomposite Packaging Materials. In *Trends in Beverage Packaging*. Elsevier, pp. 191–241.
- Shariatnia, Z., Arabzadeh, N., Abdous, M., 2011a. Ab initio calculations on the hydrogen bonding interactions among pseudophedrinium cation isomers and methacrylic acid. *Main Group Chemistry* 10 (1), 1–16.
- Shariatnia, Z., Erben, M.F., Della Védova, C.O., Abdous, M., Azodi, S., 2011b. Hydrogen bonding interactions between α -, β -glucose, and methacrylic acid. *Structural Chemistry* 22 (6), 1347.
- Shariatnia, Z., Erben, M.F., Della Védova, C.O., 2012. DFT calculations on the hydrogen bonding interactions between adrenaline and trimethoxysilylpropylamine. *Main Group Chemistry* 11 (4), 275–284.
- Shariatnia, Z., Nikfar, Z., Gholivand, K., Abolghasemi Tarei, S., 2015. Antibacterial activities of novel nanocomposite biofilms of chitosan/phosphoramidate/Ag NPs. *Polymer Composites* vol. 36 (3), 454–466.
- Sharif, S., Abbas, G., Hanif, M., *et al.*, 2019. Mucoadhesive micro-composites: Chitosan coated halloysite nanotubes for sustained drug delivery. *Colloids and Surfaces B: Biointerfaces* 184, 110527.
- Sharma, S., Swetha, K.L., Roy, A., 2019. Chitosan-Chondroitin sulfate based polyelectrolyte complex for effective management of chronic wounds. *International Journal of Biological Macromolecules* 132, 97–108.
- Shuai, C., Yu, L., Feng, P., Gao, C., Peng, S., 2020. Interfacial reinforcement in bioceramic/biopolymer composite bone scaffold: the role of coupling agent. *Colloids and Surfaces B: Biointerfaces* 193, 111083.
- Singh, B.N., Veeresh, V., Mallick, S.P., *et al.*, 2019. Design and evaluation of chitosan/chondroitin sulfate/nano-bioglass based composite scaffold for bone tissue engineering. *International Journal of Biological Macromolecules* 133, 817–830.
- Song, W., Zeng, Q., Yin, X., *et al.*, 2018. Preparation and anticoagulant properties of heparin-like electrospun membranes from carboxymethyl chitosan and bacterial cellulose sulfate. *International Journal of Biological Macromolecules* 120, 1396–1405.
- Stanisz, M., Klapiszewski, Ł., Jesionowski, T., 2020. Recent advances in the fabrication and application of biopolymer-based micro- and nanostructures: A comprehensive review. *Chemical Engineering Journal*, 125409.
- Sun, Q., Bi, H., Wang, Z., *et al.*, 2019a. Hyaluronic acid-targeted and pH-responsive drug delivery system based on metal-organic frameworks for efficient antitumor therapy. *Biomaterials* 223, 119473.
- Sun, X., Shen, J., Yu, D., Ouyang, X.-k., 2019b. Preparation of pH-sensitive Fe₃O₄@C/carboxymethyl cellulose/chitosan composite beads for diclofenac sodium delivery. *International Journal of Biological Macromolecules* 127, 594–605.

- Tanaka, C.B., Lopes, D.P., Kikuchi, L.N.T., *et al.*, 2020. Development of novel dental restorative composites with dibasic calcium phosphate loaded chitosan fillers. *Dental Materials* 36 (4), 551–559.
- Tohamy, K.M., Mabrouk, M., Soliman, I.E., Beherei, H.H., Aboelnasr, M.A., 2018. Novel alginate/hydroxyethyl cellulose/hydroxyapatite composite scaffold for bone regeneration: *In vitro* cell viability and proliferation of human mesenchymal stem cells. *International Journal of Biological Macromolecules* 112, 448–460.
- Torkashvand, N., Sarlak, N., 2019. Fabrication of a dual T1 and T2 contrast agent for magnetic resonance imaging using cellulose nanocrystals/Fe₃O₄ nanocomposite. *European Polymer Journal* 118, 128–136.
- Ul-Islam, M., Subhan, F., Islam, S.U., *et al.*, 2019. Development of three-dimensional bacterial cellulose/chitosan scaffolds: Analysis of cell-scaffold interaction for potential application in the diagnosis of ovarian cancer. *International Journal of Biological Macromolecules* 137, 1050–1059.
- Varaprasad, K., Jayaramudu, T., Kanikireddy, V., Toro, C., Sadiku, E.R., 2020. Alginate-based composite materials for wound dressing application: A mini review. *Carbohydrate Polymers* 236, 116025.
- Vasvani, S., Kulkarni, P., Rawtani, D., 2020. Hyaluronic acid: A review on its biology, aspects of drug delivery, route of administrations and a special emphasis on its approved marketed products and recent clinical studies. *International Journal of Biological Macromolecules* 151, 1012–1029.
- Vatanparast, M., Shariatinia, Z., 2018a. AIN and AIP doped graphene quantum dots as novel drug delivery systems for 5-fluorouracil drug: Theoretical studies. *Journal of Fluorine Chemistry* 211, 81–93.
- Vatanparast, M., Shariatinia, Z., 2018b. Computational studies on the doped graphene quantum dots as potential carriers in drug delivery systems for isoniazid drug. *Structural Chemistry* 29 (5), 1427–1448.
- Vatanparast, M., Shariatinia, Z., 2019a. Hexagonal boron nitride nanosheet as novel drug delivery system for anticancer drugs: Insights from DFT calculations and molecular dynamics simulations. *Journal of Molecular Graphics and Modelling* 89, 50–59.
- Vatanparast, M., Shariatinia, Z., 2019b. Revealing the role of different nitrogen functionalities in the drug delivery performance of graphene quantum dots: A combined density functional theory and molecular dynamics approach. *Journal of Materials Chemistry B* 7 (40), 6156–6171.
- Vinod, A., Sanjay, M.R., Suchart, S., Jyotishkumar, P., 2020. Renewable and sustainable biobased materials: An assessment on biofibers, biofilms, biopolymers and biocomposites. *Journal of Cleaner Production* 258, 120978.
- Wang, X., Xu, L., Ren, Z., *et al.*, 2019a. A novel manganese chelated macromolecular MRI contrast agent based on O-carboxymethyl chitosan derivatives. *Colloids and Surfaces B: Biointerfaces* 183, 110452.
- Wang, F., Zhang, Q., Li, X., *et al.*, 2019b. Redox-responsive blend hydrogel films based on carboxymethyl cellulose/chitosan microspheres as dual delivery carrier. *International Journal of Biological Macromolecules* 134, 413–421.
- Wang, Y., Liu, G., Wu, L., *et al.*, 2020. Rational design of porous starch/hyaluronic acid composites for hemostasis. *International Journal of Biological Macromolecules* 158, 1319–1329.
- Wei, Z., Volkova, E., Blatchley, M.R., Gerecht, S., 2019. Hydrogel vehicles for sequential delivery of protein drugs to promote vascular regeneration. *Advanced Drug Delivery Reviews* 149–150, 95–106.
- Wsoo, M.A., Shahir, S., Mohd Bohari, S.P., Nayan, N.H.M., Razak, S.I.A., 2020. A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective. *Carbohydrate Research* 491, 107978.
- Wu, D., Yu, Y., Tan, J., *et al.*, 2018. 3D bioprinting of gellan gum and poly (ethylene glycol) diacrylate based hydrogels to produce human-scale constructs with high-fidelity. *Materials & Design* 160, 486–495.
- Xie, M., Zhang, F., Liu, L., *et al.*, 2018. Surface modification of graphene oxide nanosheets by protamine sulfate/sodium alginate for anti-cancer drug delivery application. *Applied Surface Science* 440, 853–860.
- Xu, J., Tan, X., Chen, L., Li, X., Xie, F., 2019. Starch/microcrystalline cellulose hybrid gels as gastric-floating drug delivery systems. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 215. Elsevier, pp. 151–159.
- Xu, W., Lou, Y., Xu, B., *et al.*, 2018. Mineralized calcium carbonate/xanthan gum microspheres for lysozyme adsorption. *International Journal of Biological Macromolecules* 120, 2175–2179.
- Ye, S., Jiang, L., Su, C., *et al.*, 2019. Development of gelatin/bacterial cellulose composite sponges as potential natural wound dressings. *International Journal of Biological Macromolecules* 133, 148–155.
- Yuan, S., Shen, F., Chua, C.K., Zhou, K., 2019. Polymeric composites for powder-based additive manufacturing: materials and applications. *Progress in Polymer Science* 91, 141–168.
- Zamani, D., Moztaazadeh, F., Bizari, D., 2019. Alginate-bioactive glass containing Zn and Mg composite scaffolds for bone tissue engineering. *International Journal of Biological Macromolecules* 137, 1256–1267.
- Zhang, L.-K., Du, S., Wang, X., *et al.*, 2019. Bacterial cellulose based composites enhanced transdermal drug targeting for breast cancer treatment. *Chemical Engineering Journal* 370, 749–759.
- Zhao, Y., He, M., Jin, H., *et al.*, 2018. Construction of highly biocompatible hydroxyethyl cellulose/soy protein isolate composite sponges for tissue engineering. *Chemical Engineering Journal* 341, 402–413.
- Zhou, L., Xu, T., Yan, J., *et al.*, 2020. Fabrication and characterization of matrine-loaded konjac glucomannan/fish gelatin composite hydrogel as antimicrobial wound dressing. *Food Hydrocolloids* 104, 105702.
- Zhou, P., Xia, Y., Cheng, X., *et al.*, 2014. Enhanced bone tissue regeneration by antibacterial and osteoinductive silica-HACC-zein composite scaffolds loaded with rhBMP-2. *Biomaterials* 35 (38), 10033–10045.
- Zhou, X., Wang, J., Fang, W., *et al.*, 2018. Genipin cross-linked type II collagen/chondroitin sulfate composite hydrogel-like cell delivery system induces differentiation of adipose-derived stem cells and regenerates degenerated nucleus pulposus. *Acta Biomaterialia* 71, 496–509.
- Zulkifli, F.H., Hussain, F.S.J., Harun, W.S.W., Yusoff, M.M., 2019. Highly porous of hydroxyethyl cellulose biocomposite scaffolds for tissue engineering. *International Journal of Biological Macromolecules* 122, 562–571.
- Zulkifli, F.H., Hussain, F.S.J., Zeyohannes, S.S., Rasad, M.S.B.A., Yusuff, M.M., 2017. A facile synthesis method of hydroxyethyl cellulose-silver nanoparticle scaffolds for skin tissue engineering applications. *Materials Science and Engineering C* 79, 151–160.

Poly(methyl methacrylate)-Based Composite Bone Cements With Different Types of Reinforcement Agents

Sanaz Soleymani Eil Bakhtiari, Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

Hamid Reza Bakhsheshi-Rad, Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran and Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Saeed Karbasi, Biomaterials and Tissue Engineering Department, School of Advanced Technologies in Medicine, Isfahan University of Medical Sciences, Isfahan, Iran

Ahmad Fauzi Ismail, Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Safian Sharif, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Alexander Seifalian, Nanotechnology and Regenerative Medicine Commercialisation Centre (NanoRegMed Ltd), London BioScience Innovation Centre, London, United Kingdom

Houman Savoji, Institute of Biomedical Engineering, Department of Pharmacology and Physiology, Faculty of Medicine, University of Montreal, CHU Sainte Justine Research Center, Montreal TransMedTech Institute, Montreal, QC, Canada

Filippo Berto, Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway

© 2021 Elsevier Inc. All rights reserved.

Introduction

Acrylic acid was first discovered in 1843 and then led to the formulation of methacrylic acid (MA) in 1865 (Hendriks *et al.*, 2004). The chemical reaction of MA with methanol leads to the formation of methyl methacrylate (MMA), which is the constitutional monomer of poly(methyl methacrylate) (PMMA) (Markatos *et al.*, 2010; Breusch and Malchau, 2005). PMMA was first utilized in arthroplasty by the Judet brothers in the 1950s when they fabricated femoral heads from PMMA (Judet and Judet, 1950), even though it was failed biologically and mechanically (Breusch and Malchau, 2005; Ayre, 2013). In 1953, utilizing PMMA as a grout for enhancing the implant fixation in bone (Haboush, 1953) was followed by Sir John Charnley in 1958, who succeeded to anchor a femoral head prosthesis in a femur through auto-polymerization of PMMA (Charnley, 1960). This eventuated in an entirely novel surgical technique whereby acetabular and femoral implants could be fixed to the bone by PMMA during hip replacements (Charnley, 1970). Today, loading antibiotics such as gentamicin, penicillin, and erythromycin in cement is still followed with gentamicin in bone cements (BCs) (Ayre, 2013; Buchholz, 1970; Soleymani Eil Bakhtiari *et al.*, 2020b). Commercial PMMA-based BCs consist of two phases, including a liquid monomer and a solid powder, in which their combination leads to form polymer chains through a free-radical polymerization process. In commercially available PMMA-based BCs, the liquid phase contains MMA, N,N-Dimethyl-p-Toluidine (DMPT) as an activator, and a small amount of hydroquinone as a polymerization inhibitor for the monomers during storage. The powder component consists of PMMA polymer particle, barium sulphate (BaSO_4), or zirconium dioxide (ZrO_2) as a radiopaque factor for visibility under X-ray imaging and benzoyl peroxide (BPO) as an initiator for the polymerization reaction (Kuehn *et al.*, 2005). This kind of BCs is a polymeric material that presents great cytocompatibility and offers outstanding preliminary fixation among bone and implant. Nevertheless, it has certain drawbacks such as escalating in temperature throughout the polymerization, which might result in bone cell necrosis as well as implant loosening and inadequate mechanical characteristics, lack of bone formation, and bioactivity, which often may lead to failure of the bone cement (BC). As a consequence of the high utilization of BCs, numerous researchers have made attempts to remove the issues of BCs. To be able to enhance and restore the PMMA-based BCs, several ceramic, polymer, and composite reinforcement agents have been employed. Despite the fact that numerous articles are previously published concerning PMMA-based BC (Dunne and Ormsby, 2011; Ormsby *et al.*, 2010; Huang *et al.*, 2005) a few articles are observed, which specifically examined PMMA-based composite BCs with various kinds of additive agents for orthopedic applications. This study describes PMMA-based BC development in the previous years concerning filler for skull bone and bone cavity. On top of that, we will review the latest advancements based on the kind of additive agent employed for preparing PMMA-based composite BCs. In addition the effect of carbon based materials incorporation on the mechanical and cellular response of BCs, comparing their effectiveness was reviewed in this study, which is barely studied before. The purpose is to depict the demands of the right choice of additives agents for PMMA-based BCs, so we will realize the current status and understand the forthcoming requirements of this field. Fig. 1 shows the chemical structure of MMA liquid and PMMA powder in the PMMA-based BCs (Dunne *et al.*, 2014).

Properties of the PMMA-Based BCs

Handling Properties

Four different phases can describe the curing process of the PMMA-based BCs with their related viscosities, including mixing, waiting, working or application, and hardening or setting (Dunne and Orr, 2002; Lewis, 2003). The *mixing phase*, which takes up to 1 min, is the time for the entire homogenization of the polymer powder with the liquid components. The *waiting phase* lasts up to

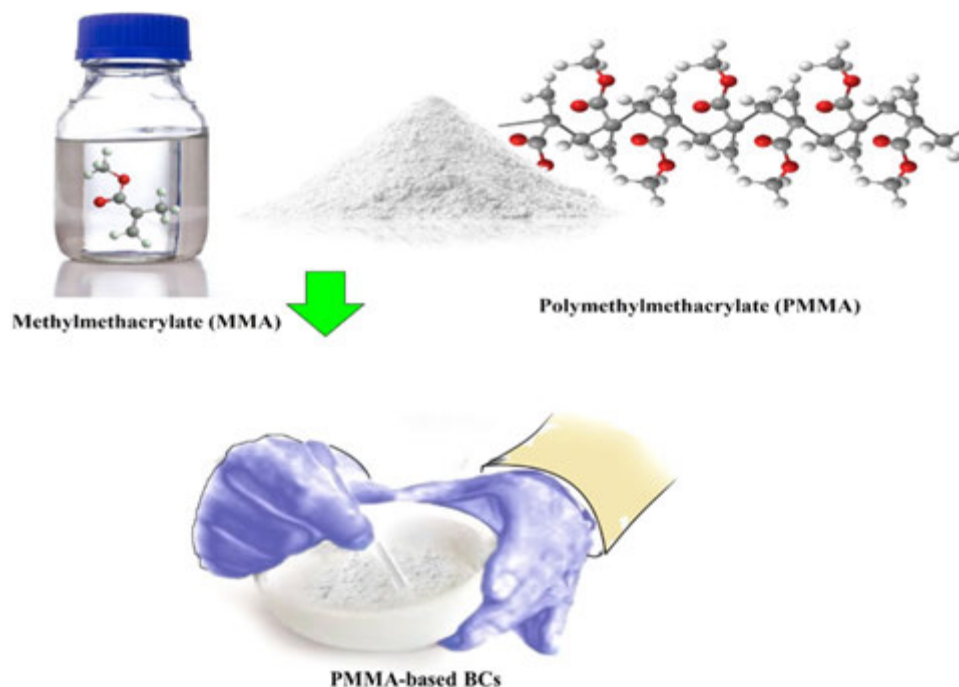


Fig. 1 Chemical structures of MMA liquid and PMMA powder in the PMMA-based BCs. Adapted from Dunne, N., Clements, J., Wang, J.S., 2014. Acrylic cements for bone fixation in joint replacement. In: Joint Replacement Technology. Woodhead Publishing, pp. 212–256.

several minutes. The cement turns into a non-sticky state at this stage, thus, ready to use. In the *working or application phase*, which lasts 2–4 min depending on the type of BC and curing temperature, the cement is injected into the bone prior to implantation of the prosthesis. The *hardening or setting phase*, which lasts 1–2 min, is the last stage leading to an exothermic polymerization interaction producing heat. At the end of the setting phase, the heat produced through polymerization will drop back to ambient temperature (Dunne *et al.*, 2014; Soleymani Eil Bakhtiari *et al.*, 2020a).

Thermal Properties

Once the liquid and powder components are mixed, BPO reacts with *N,N*-DMPT to create free radicals, called the “initiation reaction”, leading to polymerizing MMA into PMMA through incorporating the polymerizable double-bond of the monomer molecule (Dunne and Ormsby, 2011; Huang *et al.*, 2005; Soleymani Eil Bakhtiari *et al.*, 2020b). Exothermicity is significantly critical for the process of polymerization. The point that the heat rises connected to the cement mantle thickness, the room temperature, and the weight percentage of polymer to monomer has been shown *in vitro*. The calculated value range between 70 and 120°C; but then again, the *in vivo* examination exhibited are luckily the minimum value between 40 and 56°C, reflecting the threshold values beyond which may induce protein coagulation with associated biological destruction (osteonecrosis) (Magnan *et al.*, 2013; Webb and Spencer, 2007). The *in vivo* thermogenesis of BCs may lead to thermal necrosis of the bone cells and cell damage in the binding sites, which may cause a premature failure through the aseptic loosening of the implant (Dunne and Ormsby, 2011; Huang *et al.*, 2005). Setting properties of BCs are carried out according to the ISO5833:2002 and ASTM F451–99a standards (Standard, 2002, 2006).

Mechanical Properties

PMMA-based BCs mainly present an anisotropic mechanical function through evenly distributing and transferring the mechanical stresses from the implant to the bone (Charnley, 1970; Dunne *et al.*, 2014). Clinical cement from PMMA is brittle in nature. It is fragile in stress, like other brittle components, but very strong under compression. Typically, compressive strength ranges from 44 to 103 MN/m². This really is about 50%–70% of the cortical bone’s mechanical property. The elasticity modulus is stated to have ranged from 2140–3100 MN/m². The intensity of this module was almost one order lower than the average cortical bone. The amounts’ differences are primarily attributed to the variations in the loading rate or strain during testing and the elements connected with the sample preparation process. PMMA-based BC is employed to restore pathological bone injuries and bony disorders when subjected to bending impact. Hence it is beneficial to find out its bending or flexural strength for the development of such clinical use (Saha and Pal, 1984). Determining the compressive, bending and fracture toughness properties of PMMA-based BCs are performed according to ISO5833:2002, ASTM F451–99a and ASTM E399 standards (Standard, 2002, 2006, 1989).

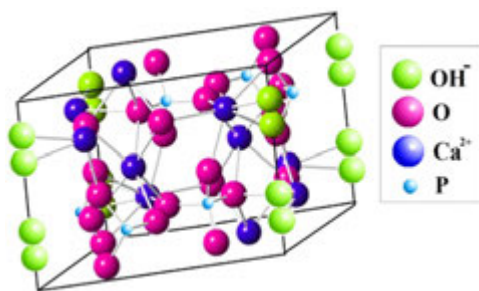


Fig. 2 Chemical structure of HA. Adapted from Mostafa, N.Y., Brown, P.W., 2007. Computer simulation of stoichiometric hydroxyapatite: Structure and substitutions. *Journal of Physics and Chemistry of Solids* 68 (3), 431–437.

Biological Properties

Since PMMA-based BCs are biologically inert, they do not contribute to the surrounding bone's growth and regeneration. Thus cement-bone interface connection is weak. Several studies attempted to enhance the biocompatibility of BC. To enhance cytocompatibility and apatite formation ability of PMMA surface when it is exposed to the bone environment, the bioactive phases such as hydroxyapatite (HA) (Kim *et al.*, 2004; Wolf-Brandstetter *et al.*, 2013) or bioglass (Heikkilä *et al.*, 1996; Rhee *et al.*, 2003; Shinzato *et al.*, 2004; Wolf-Brandstetter *et al.*, 2013) encapsulated into the PMMA-based BC. The purpose was to have the bone nearer to the cemented implant and thereby to minimize micromotions that are considered necessary for recovery and stabilization (Sundfeldt *et al.*, 2006). For clinical success, the contact between the metal implant surface and the BC also plays a crucial role (Jasty *et al.*, 1991; Wolf-Brandstetter *et al.*, 2013). Incorporating bioactive agents in formulation leading to an enhancement in the biocompatibility of BCs, thus reducing the formation of fibrous tissue at the bone-cement interface (Dunne and Ormsby, 2011; Jimenez, 2017).

Current Problems Related to the PMMA-Based BCs

Although PMMA-based BCs have desirable properties such as appropriate biocompatibility and excellent initial fixation between bone and implant, they have some drawbacks such as lack of bone formation, lack of bioactivity, and poor mechanical properties leading to failure the BCs. In order to enhance the mechanical, biological, and bioactivity properties of PMMA-based BCs, many researchers have made efforts to resolve their weakness through adding different kinds of ceramic, polymer, or a composite of them as reinforcements. The most common reinforcements used to improve PMMA-based BCs are discussed below.

Different Types of Reinforcements in the PMMA-Based Composite BCs

Hydroxyapatite (HA)

In human bone tissue, HA possesses a comparable chemical property to apatite and can join the host bone tissue (Harakas, 1984; Quan *et al.*, 2016). The additive phase incorporated into PMMA-based BC broadly to escalate cell viability and bioactivity (Kalita *et al.*, 2007; Quan *et al.*, 2016). The chemical structure of HA is shown in Fig. 2 (Mostafa and Brown, 2007). HA powder is an appropriate reinforcement for organic polymers, mechanically, and biologically. HA is a biocompatible, osteoconductive, and osteophilic biomaterial (Ogiso, 1992). It is reported that HA particles can present a bone formation due to an ingrowth in bone-forming cells when they were placed next to a viable bone. Various authors have reported encouraging results about adding particulate HA to commercial BCs (Lee *et al.*, 1997; Liebendörfer *et al.*, 1995; Perek and Pilliar, 1992; Harper *et al.*, 1995; Soleymani Eil Bakhtiari *et al.*, 2020b).

Carbon-Based Nanomaterials (CBNs)

Carbon nanotubes (CNTs) and graphene oxide (GO) are the most popular CBNs (Rajakumar *et al.*, 2020; Cha *et al.*, 2013). CNTs, discovered by the Japanese scientist Iijima in 1991 (Iijima, 1991), are now turned to a top-class subject either in academic researches and other industrial areas. This kind of carbon allotropy, composed of graphite, has been produced in cylindrical tubes with a diameter in a nanometer scale and a length in several micrometers (Hirlekar *et al.*, 2009; Singh *et al.*, 2012). CNTs structures are classified into two types depending on the number of layers, including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Their desirable and specific structural, mechanical, and electronic properties are related to their tiny size, light mass, high mechanical strength, electrical and thermal conductivity (Usui *et al.*, 2012; Zhang *et al.*, 2010; Soleymani Eil Bakhtiari *et al.*, 2019). Another important CBNs is GO. In specific, due to its favorable aqueous durability,

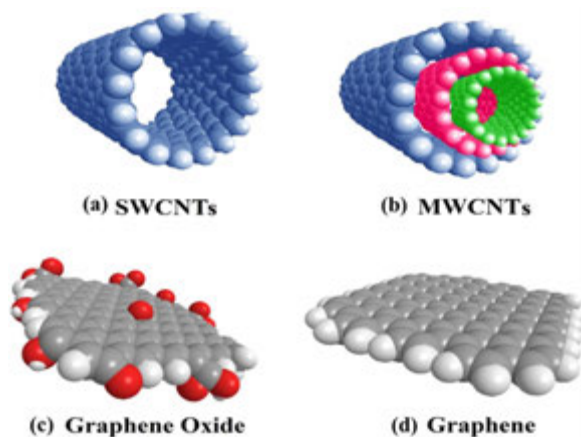


Fig. 3 Structure of (a) SWCNTs (b) MWCNTs (c) GO (d) Graphene sheet. Adapted from Ahmed, N., Khan, U., Mohyud-Din, S.T., 2020. Modified heat transfer flow model for SWCNTs-H₂O and MWCNTs-H₂O over a curved stretchable semi infinite region with thermal jump and velocity slip: A numerical simulation Physica A: Statistical Mechanics and its Applications 545, 123431. Doi, Y., Nakatani, A., 2011. Structure and stability of nonlinear vibration mode in graphene sheet. Procedia Engineering 10, 3393–3398.

amphiphilicity, surface functionality and property, and fluorescence quenching capacity, GO chemically exfoliated from oxidized graphite is regarded as a viable component for biological purposes (Chung *et al.*, 2013). GO can have appropriate physical and chemical interactions with biopolymers. Moreover, it has appropriate biocompatibility to consume in medicine due to its carbonyl, carboxyl, and hydroxyl groups (Tavakoli and Karbasi, 2020b; Depan *et al.*, 2014; Soleymani Eil Bakhtiari *et al.*, 2020a). It is reported that the three carbon nanostructures, including CNTs, graphene (G), and GO play an important role in cell behavior and mechanical properties (Soleymani Eil Bakhtiari *et al.*, 2019; Liu-Snyder and Webster, 2008; Novoselov *et al.*, 2004; Compton and Nguyen, 2010; Lam *et al.*, 2004; Pahlevanzadeh *et al.*, 2019a; Soleymani Eil Bakhtiari *et al.*, 2020a). The structures of CNTs, GO, and G sheet are shown in Fig. 3 (Ahmed *et al.*, 2020; Doi and Nakatani, 2011).

Chitosan

Chitosan (CS) is another reinforcement used in the PMMA-based BCs. CS, as one of the most functional polymers, is a natural linear polysaccharide derived from chitin. It can be extracted from the exoskeletons of shrimp, crab, and the cell wall of fungi (Soleymani Eil Bakhtiari *et al.*, 2019; Jaafari *et al.*, 2004). The chemical structure of chitin and CS are shown in Fig. 4 (Kumar, 2000). CS is a biodegradable copolymer composed of N-acetyl glucosamine and D-glucosamine (Yuan *et al.*, 2010). It is a biomaterial used in medical applications due to its desirable properties such as low toxicity, excellent biocompatibility, biodegradability, anticoagulation, wound healing, and antibacterial properties (Jayakumar *et al.*, 2011; Venkatesan and Kim, 2010; Parvizifard *et al.*, 2020). The effects of CS on the PMMA-based BCs are reported in many studies. Intramolecular hydrogen bonds existed in CS provide a series of reactive heat resistance macromolecules (Endogan *et al.*, 2014).

Effect of Different Reinforcements on Setting Properties

The effect of different reinforcements on the setting process of the PMMA-based composite BCs are tabulated in Table 1. According to the table, the setting properties of PMMA-based composite BCs including HA, glass ceramic (GC), HA/CS, MWCNTs, functionalized MWCNTs (f-MWCNTs), CS, quaternized CS, GO, CS/MWCNTs, CS/GO, CS/ β -tricalcium phosphate (β -TCP), SiO₂, SiO₂/Tri-calcium phosphate (TCP), SiO₂/hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA), TCP/CS, polycaprolactone (PCL), PCL/baghdadite (BAGH), MgO, calcium silicate, cellulose, Mg, polydioxanone (PDO) and sodium polyacrylate short fibers (PAAS_f) were evaluated.

In a study by Samad *et al.* (2011) application of new bioactive GC in PMMA-based BCs was evaluated. The obtained results showed as the concentration of the reinforcement phase (HA and GC) amplified, the peak temperature throughout the setting response diminished and all filled BCs presented a lower peak temperature compared with the reference specimen, but overall PMMA-based BCs containing 4 and 8 wt% GC filler loading exhibited optimum setting and handling properties (Samad *et al.*, 2011). In another study Ferreira *et al.* (2014) evaluated the properties of novel PMMA-based BCs filled with HA. According to the results obtained from adding 25 wt% HA to the PMMA-based BC, it can be concluded that the partial substitution of commercial PMMA beads by commercial HA decreases the values of peak temperature while increases the setting time (Ferreira *et al.*, 2014). In other study by Kim *et al.* (2004), the characteristics of PMMA-HA/CS-based BCs were investigated. It was reported that a decreased thermogenesis and an increased setting time can be achieved in the PMMA-HA/CS-based BCs in comparison with a pure PMMA-based BC (Kim *et al.*, 2004). In a study by Ormsby *et al.* (2010), the effects of MWCNTs on mechanical and thermal properties of

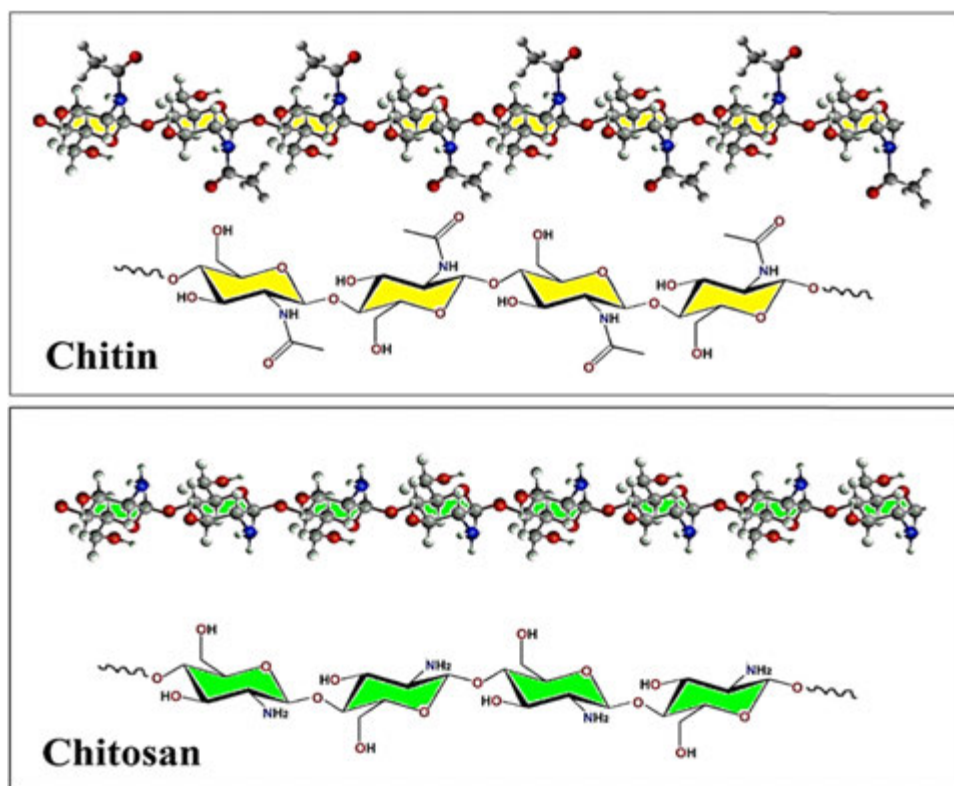


Fig. 4 Chemical structures of Chitin and Chitosan. Adapted from Kumar, M.N., 2000. A review of chitin and chitosan applications. *Reactive and Functional Polymers* 46 (1), 1–27.

PMMA-based BCs were evaluated. Obtained results showed that adding the thermally conductive *f*-MWCNTs to the PMMA-based BCs significantly reduced the heat produced in the exothermic polymerization reaction of the BCs and they also significantly increased the setting time of BCs (Ormsby *et al.*, 2010; Soleymani Eil Bakhtiari *et al.*, 2020a). In another study, Endogan *et al.* (2014) evaluated the effects of the PMMA powder size and CS addition on the properties of PMMA-based BCs. Obtained results showed that adding CS to the PMMA-based BCs containing PMMA powder with particle size in the range of 50–150 μm , leads to a decrease in polymerization temperature (Endogan *et al.*, 2014). In other study by Tan *et al.* (2012), novel PMMA/quaternized CS-based BC was fabricated and its setting properties were evaluated. The results of PMMA/quaternized CS-based BC presented modified properties such as a lower curing temperature and more prolonged setting time in comparison with other PMMA-based BCs (Tan *et al.*, 2012). Valencia Zapata *et al.* (2020) and Zapata *et al.* (2020) fabricated cement containing CS for biomedical fields. Their result exhibited the alteration of setting characteristics, such as reduced maximum temperature and escalation in setting time (Valencia Zapata *et al.*, 2020; Zapata *et al.*, 2020). In this regard, throughout the MMA polymerization reaction, the maximum temperature attained showed a diminishing of 13°C with a 20% CS loading, and the increase in setting time was significant for formulations with CS loading ≥ 15 wt% (Valencia Zapata *et al.*, 2020). The incorporation of CS and GO individually or jointly in BC composition, likewise elevated setting characteristics (Zapata *et al.*, 2020). The reduction in the maximum temperature with an enhancement in CS encapsulation results from the heat sink serving as intramolecular hydrogen bonds in CS (Endogan *et al.*, 2014). In another studies by Soleymani Eil Bakhtiari *et al.* (2020c) and Tavakoli *et al.* (2020a) the effects of CS powder, CS/MWCNTs and CS/GO composite powder on physical, mechanical and biological properties of PMMA-based BCs were investigated. Obtained results showed that adding CS powder, CS/MWCNTs and CS/GO composite powder to the PMMA-based BCs increased setting time and decreased maximum temperature, significantly (Soleymani Eil Bakhtiari *et al.*, 2020a,c; Tavakoli *et al.*, 2020a). In other study by Lin *et al.* (2005), the effects of CS/ β -TCP microspheres on setting and mechanical properties of PMMA-based BCs were evaluated. Obtained results of the PMMA/CS- β -TCP-based BCs showed that adding CS/ β -TCP in the form of microspheres significantly decreased the maximum curing temperature and delayed the final cure, thus more manipulating time for the operation (Lin *et al.*, 2005). In other study by Yang *et al.* (1997), PMMA/SiO₂-based BCs containing different reinforcements were fabricated. Obtained results showed that in PMMA/SiO₂-based composite BCs, adding TCP to the BCs led to an increase in setting time and decrease in maximum curing temperature, while adding HEMA and EGDMA to the PMMA/SiO₂-based BCs reversely affected the BCs (Yang *et al.*, 1997). In another study (Tsukeoka *et al.*, 2006), modifying PMMA-based BCs by γ -methacryloxypropyltrimethoxysilane (MPS) and calcium acetate presented an increased setting time, while a lower curing temperature (Tsukeoka *et al.*, 2006). In another study by Fang *et al.* (2019), PMMA-based composite BCs containing TCP/CS were prepared. Obtained results indicated that by adding TCP/CS to the PMMA-based BCs, the curing temperature of BCs was

Table 1 Setting properties of PMMA-based composite BCs containing different types of reinforcements

Sample of BCs	Maximum temperature (°C)	Setting time (sec)	Reference
PMMA	52.90	740.40	(Samad <i>et al.</i> , 2011)
PMMA/4 wt% HA	47.60	780.00	(Samad <i>et al.</i> , 2011)
PMMA/8 wt% HA	44.90	717.60	(Samad <i>et al.</i> , 2011)
PMMA/12 wt% HA	44.90	840.00	(Samad <i>et al.</i> , 2011)
PMMA/16 wt% HA	43.40	798.00	(Samad <i>et al.</i> , 2011)
PMMA/4 wt% GC	47.20	844.20	(Samad <i>et al.</i> , 2011)
PMMA/8 wt% GC	45.10	765.00	(Samad <i>et al.</i> , 2011)
PMMA/12 wt% GC	38.10	945.00	(Samad <i>et al.</i> , 2011)
PMMA/16 wt% GC	39.10	915.00	(Samad <i>et al.</i> , 2011)
PMMA	76.30 ± 2.70	540 ± 18	(Kim <i>et al.</i> , 2004)
PMMA-40 wt% HA/10 wt% CS	60.40 ± 4.80	840 ± 24	(Kim <i>et al.</i> , 2004)
PMMA-50 wt% HA/10 wt% CS	53.50 ± 2.00	1098 ± 30	(Kim <i>et al.</i> , 2004)
PMMA-60 wt% HA/10 wt% CS	49.90 ± 1.50	1218 ± 36	(Kim <i>et al.</i> , 2004)
PMMA	91.90 ± 6.00	694 ± 3.00	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% MWCNTs (Magnetic stirring)	65.17 ± 1.90	1260 ± 5.40	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% f-MWCNTs (Magnetic stirring)	43.42 ± 2.00	2131 ± 4.00	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% MWCNTs (Dry blending)	76.40 ± 9.60	1364 ± 8.20	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% f-MWCNTs (Dry blending)	68.53 ± 6.00	1712 ± 7.00	(Ormsby <i>et al.</i> , 2010; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA/0.1 wt% MWCNTs (Ultrasonic disintegration)	83.10 ± 7.70	1054 ± 8.40	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% f-MWCNTs (Ultrasonic disintegration)	84.50 ± 4.00	1082 ± 2.00	(Ormsby <i>et al.</i> , 2010)
PMMA (Particle size range: 50–150 µm)	71.60 ± 9.31	312 ± 17	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 50–150 µm)	68.58 ± 8.92	253 ± 28	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.1 g/g) (Particle size range of PMMA: 50–150 µm)	59.04 ± 9.59	274 ± 19	(Endogan <i>et al.</i> , 2014)
PMMA (Particle size range: 0–50 µm)	83.48 ± 7.35	190 ± 20	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 0–50 µm)	85.40 ± 4.73	174 ± 7	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.1 g/g) (Particle size range of PMMA: 0–50 µm)	86.78 ± 3.73	180 ± 11	(Endogan <i>et al.</i> , 2014)
PMMA (Particle size range: 1 µm)	116.24 ± 4.94	406 ± 8	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 1 µm)	123.12 ± 4.16	456 ± 34	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.1 g/g) (Particle size range of PMMA: 1 µm)	116.32 ± 5.14	395 ± 32	(Endogan <i>et al.</i> , 2014)
PMMA	64.00 ± 2.00	352.20 ± 30.00	(Tan <i>et al.</i> , 2012)
PMMA/CS	59.67 ± 3.06	607.80 ± 9.00	(Tan <i>et al.</i> , 2012)
PMMA/Gentamicin	60.00 ± 2.00	481.80 ± 45.60	(Tan <i>et al.</i> , 2012)
PMMA/Quaternized CS	58.67 ± 0.58	655.80 ± 42.60	(Tan <i>et al.</i> , 2012)
PMMA	59 ± 3	355 ± 30	(Valencia Zapata <i>et al.</i> , 2020; Zapata <i>et al.</i> , 2020)
PMMA-5 wt% CS	58 ± 2	370 ± 15	(Valencia Zapata <i>et al.</i> , 2020)
PMMA-10 wt% CS	54 ± 3	420 ± 15	(Valencia Zapata <i>et al.</i> , 2020)
PMMA-15 wt% CS	54 ± 4	460 ± 20	(Valencia Zapata <i>et al.</i> , 2020; Zapata <i>et al.</i> , 2020)
PMMA-20 wt% CS	46 ± 2	545 ± 25	(Valencia Zapata <i>et al.</i> , 2020)
PMMA-0.3 wt% GO	51 ± 4	420 ± 25	(Zapata <i>et al.</i> , 2020)
PMMA-0.3 wt% GO-15 wt% CS	46 ± 3	440 ± 10	(Zapata <i>et al.</i> , 2020)
PMMA	74.83 ± 4.78	679.80 ± 72.00	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-20 wt% CS	71.37 ± 1.30	739.80 ± 13.80	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-20 wt% (CS/MWCNTs)	62.73 ± 3.37	930 ± 24.00	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-25 wt% CS	66.13 ± 2.56	780.00 ± 30.00	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-25 wt% (CS/MWCNTs)	58.10 ± 2.77	970.20 ± 48.00	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020a,c)
PMMA-30 wt% CS	63.27 ± 3.23	840.00 ± 24.00	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-30 wt% (CS/MWCNTs)	51.67 ± 2.04	1,030.2 ± 51.00	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA	73.80 ± 3.20	667.80 ± 19.20	(Tavakoli <i>et al.</i> , 2020a)
PMMA-20 wt% CS	67.90 ± 1.70	731.40 ± 34.20	(Tavakoli <i>et al.</i> , 2020a)
PMMA-20 wt% (CS/GO)	66.60 ± 1.50	734.40 ± 18.60	(Tavakoli <i>et al.</i> , 2020a)

Table 1 Continued

Sample of BCs	Maximum temperature (°C)	Setting time (sec)	Reference
PMMA-25 wt% CS	61.60 ± 2.60	751.20 ± 16.80	(Tavakoli <i>et al.</i> , 2020a)
PMMA-25 wt% (CS/GO)	62.30 ± 1.90	768.00 ± 20.40	(Tavakoli <i>et al.</i> , 2020a; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA-30 wt% CS	60.80 ± 2.90	777.60 ± 16.20	(Tavakoli <i>et al.</i> , 2020a)
PMMA-30 wt% (CS/GO)	60.00 ± 1.90	787.80 ± 6.00	(Tavakoli <i>et al.</i> , 2020a)
PMMA	≈ 41.50	210	(Lin <i>et al.</i> , 2005)
PMMA/50 wt% (CS-β-TCP) (Electrostatic system)	≈ 27.00	420	(Lin <i>et al.</i> , 2005)
PMMA/66.7 wt% (CS-β-TCP) (Electrostatic system)	≈ 28.00	540	(Lin <i>et al.</i> , 2005)
PMMA/50 wt% (CS-β-TCP) (Emulsion technique)	≈ 35.00	360	(Lin <i>et al.</i> , 2005)
PMMA/66.7 wt% (CS-β-TCP) (Emulsion technique)	≈ 27.50	480	(Lin <i>et al.</i> , 2005)
PMMA/SiO ₂	69	579	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /50 wt% TCP	60	709	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /15 wt% HEMA	77	368	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /15 wt% HEMA/0.6 wt% EGDMA	81	287	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /50 wt% TCP/15 wt% HEMA/0.6 wt% EGDMA	78	350	(Yang <i>et al.</i> , 1997)
PMMA	82.50 ± 0.60	720 ± 24	(Tsukeoka <i>et al.</i> , 2006)
Modified PMMA	51.00 ± 1.20	1086 ± 138	(Tsukeoka <i>et al.</i> , 2006)
PMMA	72.00	450	(Fang <i>et al.</i> , 2019)
PMMA/16.25 wt% TCP/8.75 wt% CS	70.50	462	(Fang <i>et al.</i> , 2019)
PMMA/21.71 wt% TCP/11.69 wt% CS	68.00	492	(Fang <i>et al.</i> , 2019)
PMMA/32.5 wt% TCP/17.5 wt% CS	56.00	672	(Fang <i>et al.</i> , 2019)
PMMA/43.29 wt% TCP/23.31 wt% CS	44.50	780	(Fang <i>et al.</i> , 2019)
PMMA/48.75 wt% TCP/26.25 wt% CS	43.50	900	(Fang <i>et al.</i> , 2019)
PMMA-PCL	89.60 ± 3.10	810 ± 12	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL/20 wt% BAGH	86.70 ± 2.80	834 ± 18	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL/40 wt% BAGH	82.10 ± 2.40	852 ± 18	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL/60 wt% BAGH	73.50 ± 1.90	906 ± 24	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA	64.42	573.00	(Khandaker and Meng, 2015)
PMMA/2 wt% MgO (with MMA monomer)	58.91	558.60	(Khandaker and Meng, 2015)
PMMA	≈ 54	≈ 1350 (initial) ≈ 1650 (final)	(Sun <i>et al.</i> , 2019)
PMMA/10 wt% Calcium Silicate	≈ 50	≈ 1200 (initial) ≈ 1470 (final)	(Sun <i>et al.</i> , 2019)
PMMA/20 wt% Calcium Silicate	≈ 44	≈ 1050 (initial) ≈ 1260 (final)	(Sun <i>et al.</i> , 2019)
PMMA/30 wt% Calcium Silicate	≈ 39.5	≈ 1056 (initial) ≈ 1350 (final)	(Sun <i>et al.</i> , 2019)
PMMA	38.40 ± 1.50	912.00 ± 84.00	(Wekwejt <i>et al.</i> , 2020)
PMMA/10 wt% Cellulose	35.70 ± 2.10	930.00 ± 78.00	(Wekwejt <i>et al.</i> , 2020)
PMMA/10 wt% CS	37.10 ± 2.60	918.00 ± 90.00	(Wekwejt <i>et al.</i> , 2020)
PMMA/10 wt% Mg	40.50 ± 1.80	810.00 ± 78.00	(Wekwejt <i>et al.</i> , 2020)
PMMA/10 wt% PDO	37.70 ± 1.60	966.00 ± 66.00	(Wekwejt <i>et al.</i> , 2020)
PMMA/10 wt% TCP	37.60 ± 2.20	852.00 ± 84.00	(Wekwejt <i>et al.</i> , 2020)
PMMA	83.10	774	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (9:1 vol%)	70.60	780	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (8:2 vol%)	61.20	804	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (7:3 vol%)	55.30	1128	(Tang <i>et al.</i> , 2017)

decreased, and longer setting time was achieved (Fang *et al.*, 2019). In another study by Pahlevanzadeh *et al.* (2019b) adding BAGH to the PMMA/PCL-based BCs led to an increase in setting time and decreased temperature (Pahlevanzadeh *et al.*, 2019b). In a study by Khandaker and Meng (2015) the PMMA-based BC containing 2 wt% MgO indicated a significantly lower curing temperature than other samples having MMA monomer only (Khandaker and Meng, 2015). The results obtained from the constructed PMMA/calcium silicate hybrid-based BCs showed that the curing temperature was substantially lower than the pure PMMA-based BC (Sun *et al.*, 2019). In another research carried out by Wekwejt *et al.* (2020), several modifier phases incorporated to neat PMMA-based BC, composed of cellulose, CS, Mg, PDO, and TCP. The outcomes revealed which the encapsulation of

modifiers did not tremendously impact BC's setting characteristics. All modified BCs had a curing period of 13–17 min and an maximum polymerization temperature in the range of 34–42°C (Wekwejt *et al.*, 2020). In addition, injectable PMMA-based BCs containing short fiber were prepared by Tang *et al.* (2017). The outcomes highlighted that the PMMA-based BC curing time was 12.9 min, and the maximum temperature had been 83.10°C. It is worth noting that, curing times for BCs containing short fiber amplified with the escalating short fiber amount, although the maximum temperature diminished (Tang *et al.*, 2017).

Effect of Different Reinforcements on Mechanical Properties

The mechanical properties of the PMMA-based composite BCs containing different reinforcements including HA, Brushite, HA/CS, MWCNTs, *f*-MWCNTs, CS, gentamicin/CS, CS/GO, CS/MWCNTs, CS/ β -TCP, SiO₂, SiO₂/TCP, SiO₂/HEMA, SiO₂/HEMA/ EGDMA, TCP/CS, PCL, PCL/BAGH, calcium silicate, mineralized collagen (MC), G, GO, PCL/Fluorapatite (FA), PCL/GO, PCL/FA/GO, magnesium phosphate (MgP), TiO₂, mesoporous silica nanoparticles (MSNs), gold nanoparticles (AuNPs) and PAAS_f are tabulated in Table 2.

HA as a reinforcement phase can enhance the mechanical properties of PMMA-based BCs. In the study by (Ferreira *et al.*, 2014) obtained results indicated that bending elastic modulus increased in all samples containing HA particles (Ferreira *et al.*, 2014). In a study by Aghyarian *et al.* (2014), new PMMA-HA/Brushite-based BCs were prepared for spinal augmentation. It was reported that PMMA-HA/Brushite-based BCs presented an average compressive strength of 85 MPa and flexural strength of 65 MPa, which is high mechanical strength even at high contents of calcium phosphate fillers (Aghyarian *et al.*, 2014; Soleymani Eil Bakhtiari *et al.*, 2020b). In another study by Ayatollahi *et al.* (2018), the tension-shear fracture behavior of PMMA/HA-based BCs was evaluated. The fracture behavior of PMMA/HA-based BCs affirmed that adding HA up to 10 wt% to the PMMA-based BCs lead to an increase in the fracture toughness of BCs in all modes. However pure BC showed the greatest fracture resistance among all samples (Ayatollahi *et al.*, 2018; Soleymani Eil Bakhtiari *et al.*, 2020b). In other study by Zebarjad *et al.* (2011), mechanical properties of PMMA/HA-based BCs were investigated. The compression results disclosed that the encapsulation of 2.5 wt% HA to the PMMA-based BC escalated both compressive strength and modulus, and the bending results similarly revealed that the BC containing 2.5 wt% HA presented great bending strength compared to the BC without HA (Zebarjad *et al.*, 2011; Soleymani Eil Bakhtiari *et al.*, 2020b). In another study (Kim *et al.*, 2004) mechanical assessment of PMMA-HA/CS-based BCs before degradation indicated lower ultimate compressive strength (UCS) than pure PMMA-based BC and after degradation showed both the compressive Young's modulus and UCS were significantly decreased (Kim *et al.*, 2004). In general, the enhancement of mechanical characteristics of the PMMA/HA-based composite BCs could be attributed to the uniform distribution of small amounts of the HA particles in the PMMA matrix that act as load carriers. However, the extra content of HA leads to reverse results due to the non-uniform distribution of the HA particles and subsequent agglomeration of them and weak adhesion to the matrix, thus reducing the mechanical properties (Ferreira *et al.*, 2014; Aghyarian *et al.*, 2014; Ayatollahi *et al.*, 2018; Zebarjad *et al.*, 2011; Kim *et al.*, 2004; Soleymani Eil Bakhtiari *et al.*, 2020b). MWCNTs as another reinforcement can improve the mechanical properties of PMMA-based BCs. In the study by (Ormsby *et al.*, 2010) the obtained results from mechanical tests of PMMA/MWCNTs-based BCs showed that improvements in mechanical properties which is attributed to arresting/retarding crack propagation in the BC related to the MWCNTs through bridging the crack wake along with the perpendicular direction of the crack growth. In contrast, lessening in mechanical characteristics were attributed to MWCNTs agglomerations taking place throughout the BC structure. Moreover, these agglomerations' level was relying on the technique employed to encapsulate the MWCNTs into the BC (Ormsby *et al.*, 2010; Soleymani Eil Bakhtiari *et al.*, 2020a). In another studies (Marrs, 2007; Xu *et al.*, 2013), the obtained results from PMMA/MWCNTs-based BCs, also showed that specific MWCNTs loadings could favorably improve the mechanical performance of BCs, which can be attributed to the arresting/retarding crack propagation of MWCNTs through providing a bridging effect and preventing the crack propagation (Marrs, 2007; Xu *et al.*, 2013) and obtained results from the study was done by Xu *et al.* (2013) also showed that the *f*-MWCNTs were a promising additive to improve the compressive and bending strengths of the PMMA-based BC (Xu *et al.*, 2013). CS is another common reinforcement for PMMA-based BCs. According to the obtained results from ref (Endogan *et al.*, 2014), it can be concluded that the utilization of diverse sizes of PMMA particles did not have a significant effect on the mechanical properties of BCs, but adding CS to PMMA-based BCs had a positive effect on the compressive strength (Endogan *et al.*, 2014). In another study, PMMA/CS-based BCs were prepared by Tunney *et al.* (2008) and their mechanical properties were evaluated. Obtained results indicated that after a degradation period of 7 days, a gentamicin-loaded PMMA-based BCs containing CS presented a compressive and bending properties lower than the value required by ISO, which is 70 MPa for compressive strength and 50 MPa for bending strength (Tunney *et al.*, 2008). In other study by Valencia Zapata *et al.* (2019), novel PMMA-CS/GO-based BC was fabricated. Obtained results indicated that some hydrogen-bond interaction between the CS and the GO amplified the mechanical reinforcement in the PMMA-CS/GO-based BC compared to PMMA/CS-based BC and led to a compression resistance in the BC (Valencia Zapata *et al.*, 2019). In another study Valencia Zapata *et al.* (2020) depicted that the minimum bending strength was attained just in the composition without CS. All other compositions provided the minimum bending modulus except for the composite encapsulated with 20 wt% CS and BCs with a composition containing 15 and 20 wt% CS did not experience the minimum compressive strength (Valencia Zapata *et al.*, 2020). In another study by Zapata *et al.* (2020), the addition of 15 wt% CS than that of reference BC, a mechanical characteristic such as compressive, bending strengths and bending modulus were considerably diminished ($p < 0.01$); but when 15 wt% CS was encapsulated along with 0.3 wt% GO, compressive strength lessened substantially, even though it still stayed at greater than 70 MPa, which usually is the minimum value

Table 2 Mechanical properties of PMMA-based composite BCs containing different types of reinforcements

Sample of BCs	Compressive strength (MPa)	Compressive modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Fracture toughness (K_{IC}) (MPa m ^{1/2})	Reference
PMMA	80.92 ± 2.25	1.61 ± 0.65	47.99 ± 8.53	1.71 ± 0.32	–	(Aghyarian <i>et al.</i> , 2014)
0.74 (g/ml) PMMA/0.74 (g/ml) HA	103.50 ± 3.03	1.76 ± 0.01	64.00 ± 3.11	4.19 ± 0.08	–	(Aghyarian <i>et al.</i> , 2014; Soleymani Eil Bakhtiari <i>et al.</i> , 2020b)
0.74 (g/ml) PMMA/0.74 (g/ml) Brushite	75.63 ± 2.99	1.75 ± 0.31	63.61 ± 2.18	3.68 ± 0.08	–	(Aghyarian <i>et al.</i> , 2014; Soleymani Eil Bakhtiari <i>et al.</i> , 2020b)
0.89 (g/ml) PMMA/0.44 (g/ml) HA	84.70 ± 5.83	1.63 ± 0.16	–	–	–	(Aghyarian <i>et al.</i> , 2014)
0.89 (g/ml) PMMA/0.44 (g/ml) Brushite	82.87 ± 7.22	1.78 ± 0.41	–	–	–	(Aghyarian <i>et al.</i> , 2014)
0.89 (g/ml) PMMA/0.22 (g/ml) HA	83.91 ± 6.95	1.60 ± 0.09	–	–	–	(Aghyarian <i>et al.</i> , 2014)
0.89 (g/ml) PMMA/0.22 (g/ml) Brushite	70.03 ± 8.40	1.99 ± 0.07	–	–	–	(Aghyarian <i>et al.</i> , 2014)
Pure cement (Pure mode I)	–	–	–	–	1.63 ± 0.074	(Ayatollahi <i>et al.</i> , 2018)
PMMA/5 wt% nano HA (Pure mode I)	–	–	–	–	1.24 ± 0.030	(Ayatollahi <i>et al.</i> , 2018)
PMMA/10 wt% nano HA (Pure mode I)	–	–	–	–	1.44 ± 0.067	(Ayatollahi <i>et al.</i> , 2018; Soleymani Eil Bakhtiari <i>et al.</i> , 2020b)
PMMA/15 wt% nano HA (Pure mode I)	–	–	–	–	1.12 ± 0.19	(Ayatollahi <i>et al.</i> , 2018)
Pure cement (Pure mode II)	–	–	–	–	0.95 ± 0.025	(Ayatollahi <i>et al.</i> , 2018)
PMMA/5 wt% nano HA (Pure mode II)	–	–	–	–	0.76 ± 0.023	(Ayatollahi <i>et al.</i> , 2018)
PMMA/10 wt% nano HA (Pure mode II)	–	–	–	–	0.89 ± 0.019	(Ayatollahi <i>et al.</i> , 2018)
PMMA/15 wt% nano HA (Pure mode II)	–	–	–	–	0.66 ± 0.13	(Ayatollahi <i>et al.</i> , 2018)
PMMA	188	–	65	1.80	–	(Zebarjad <i>et al.</i> , 2011)
PMMA/2.5 wt% HA	254	–	67	2.00	–	(Zebarjad <i>et al.</i> , 2011; Soleymani Eil Bakhtiari <i>et al.</i> , 2020b)
PMMA/5 wt% HA	203	–	64	1.80	–	(Zebarjad <i>et al.</i> , 2011)
PMMA/10 wt% HA	186	–	67	1.90	–	(Zebarjad <i>et al.</i> , 2011)
PMMA (Before degradation)	93.30 ± 11.30	2.00 ± 0.30	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA-40 wt% HA/10 wt% CS (Before degradation)	81.80 ± 4.50	2.40 ± 0.30	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA-50 wt% HA/10 wt% CS (Before degradation)	72.50 ± 4.60	2.30 ± 0.50	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA-60 wt% HA/10 wt% CS (Before degradation)	63.70 ± 4.50	1.50 ± 0.40	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA(After about 8 weeks of degradation)	90.90 ± 4.50	2.00 ± 0.10	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA-40 wt% HA/10 wt% CS (After about 8 weeks of degradation)	72.70 ± 3.90	2.00 ± 0.10	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA-50 wt% HA/10 wt% CS(After about 8 weeks of degradation)	69.10 ± 5.10	1.50 ± 0.20	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA-60 wt% HA/10 wt% CS (After about 8 weeks of degradation)	48.90 ± 3.40	1.20 ± 0.10	–	–	–	(Kim <i>et al.</i> , 2004)
PMMA	59.84 ± 4.52	3.006 ± 0.830	56.44 ± 7.50	3.012 ± 0.325	1.139 ± 0.29	(Ormsby <i>et al.</i> , 2010)

(Continued)

Table 2 Continued

Sample of BCs	Compressive strength (MPa)	Compressive modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Fracture toughness (K_{IC}) (MPa m ^{1/2})	Reference
PMMA/0.1 wt% MWCNTs (Magnetic stirring)	58.65 ± 4.85	2.933 ± 0.497	46.46 ± 6.78	2.770 ± 0.181	1.252 ± 0.14	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% f-MWCNTs (Magnetic stirring)	52.26 ± 4.85	3.043 ± 0.497	54.94 ± 7.28	3.221 ± 0.761	1.335 ± 0.02	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% MWCNTs (Dry blending)	61.14 ± 4.37	3.152 ± 0.348	63.63 ± 8.99	2.916 ± 0.137	1.315 ± 0.080	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% f-MWCNTs (Dry blending)	62.24 ± 3.60	3.218 ± 0.375	68.48 ± 9.39	3.261 ± 0.118	1.490 ± 0.120	(Ormsby <i>et al.</i> , 2010; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA/0.1 wt% MWCNTs(Ultrasonic disintegration)	62.11 ± 3.83	3.077 ± 0.368	57.23 ± 6.19	3.109 ± 0.292	1.259 ± 0.180	(Ormsby <i>et al.</i> , 2010)
PMMA/0.1 wt% f-MWCNTs(Ultrasonic disintegration)	67.31 ± 3.83	3.115 ± 0.253	59.61 ± 4.75	3.480 ± 0.181	1.505 ± 0.160	(Ormsby <i>et al.</i> , 2010)
PMMA	—	—	80.30 ± 6.20	3.402 ± 0.044	1.34 ± 0.18	(Marrs, 2007)
PMMA/0.5 wt% MWCNTs	—	—	85.70 ± 3.80	3.405 ± 0.044	1.28 ± 0.16	(Marrs, 2007)
PMMA/1 wt% MWCNTs	—	—	78.30 ± 7.40	3.500 ± 0.058	—	(Marrs, 2007)
PMMA/2 wt% MWCNTs	—	—	90.60 ± 3.20	3.528 ± 0.066	1.23 ± 0.22	(Marrs, 2007; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA/5 wt% MWCNTs	—	—	84.90 ± 5.60	3.823 ± 0.127	1.20 ± 0.25	(Marrs, 2007)
PMMA/10 wt% MWCNTs	—	—	85.10 ± 6.10	4.222 ± 0.099	—	(Marrs, 2007)
PMMA	74.60 ± 2.50	—	51.20 ± 2.60	—	—	(Xu <i>et al.</i> , 2013)
PMMA/0.6 wt% MWCNTs (Magnetic stirring)	76.60 ± 2.30	—	52.30 ± 2.30	—	—	(Xu <i>et al.</i> , 2013)
PMMA/0.6 wt% MWCNTs (Ultrasonic disintegration)	80.60 ± 2.10	—	54.10 ± 2.40	—	—	(Xu <i>et al.</i> , 2013)
PMMA/0.6 wt% f-MWCNTs (Magnetic stirring)	88.80 ± 2.10	—	68.20 ± 2.30	—	—	(Xu <i>et al.</i> , 2013)
PMMA/0.6 wt% f-MWCNTs (Ultrasonic disintegration)	92.90 ± 2.20	—	74.10 ± 2.20	—	—	(Xu <i>et al.</i> , 2013; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA (Particle size range: 50–150 µm)	81.51 ± 3.43	0.57 ± 0.04	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 50–150 µm)	94.04 ± 3.77	0.57 ± 0.03	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.1 g/g) (Particle size range of PMMA: 50–150 µm)	96.62 ± 4.70	0.58 ± 0.04	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA (Particle size range: 0–50 µm)	75.37 ± 7.47	0.48 ± 0.05	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 0–50 µm)	98.40 ± 6.02	0.55 ± 0.06	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.1 g/g) (Particle size range of PMMA: 0–50 µm)	89.29 ± 7.89	0.57 ± 0.02	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA (Particle size range: 1 µm)	75.96 ± 2.21	0.53 ± 0.03	—	—	—	(Endogan <i>et al.</i> , 2014)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 1 µm)	80.26 ± 6.07	0.59 ± 0.02	—	—	—	(Endogan <i>et al.</i> , 2014)

Table 2 Continued

Sample of BCs	Compressive strength (MPa)	Compressive modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Fracture toughness (K_{IC}) (MPa m ^{1/2})	Reference
PMMA/CS (0.1 g/g) (Particle size range of PMMA: 1 μ m)	81.64 $\pm$ 7.14	0.63 $\pm$ 0.02	–	–	–	(Endogan <i>et al.</i> , 2014)
PMMA/gentamicin/CS (After a degradation period of 7 days)	Lower than 70	–	Lower than 50	–	–	(Tunney <i>et al.</i> , 2008)
PMMA	$\approx$ 102.50	–	$\approx$ 55.00	$\approx$ 2.750	–	(Valencia Zapata <i>et al.</i> , 2020)
PMMA- 5 wt% CS	$\approx$ 97.50	–	$\approx$ 47.50	$\approx$ 2.625	–	(Valencia Zapata <i>et al.</i> , 2020)
PMMA-10 wt% CS	$\approx$ 87.50	–	$\approx$ 32.50	$\approx$ 2.127	–	(Valencia Zapata <i>et al.</i> , 2020)
PMMA-15 wt% CS	$\approx$ 62.50	–	$\approx$ 28.00	$\approx$ 2.125	–	(Valencia Zapata <i>et al.</i> , 2020)
PMMA-20 wt% CS	$\approx$ 30.00	–	$\approx$ 25.00	$\approx$ 1.875	–	(Valencia Zapata <i>et al.</i> , 2020)
PMMA	93.30 $\pm$ 2.20	–	48.70 $\pm$ 4.20	2.593 $\pm$ 0.178	–	(Zapata <i>et al.</i> , 2020; Valencia Zapata <i>et al.</i> , 2019)
PMMA-15 wt% CS	62.60 $\pm$ 1.10	–	32.80 $\pm$ 2.90	2.141 $\pm$ 0.212	–	(Zapata <i>et al.</i> , 2020; Valencia Zapata <i>et al.</i> , 2019)
PMMA-0.3 wt% GO	94.00 $\pm$ 0.50	–	51.80 $\pm$ 0.40	2.599 $\pm$ 0.154	–	(Zapata <i>et al.</i> , 2020; Valencia Zapata <i>et al.</i> , 2019)
PMMA-0.3 wt% GO-15 wt% CS	77.20 $\pm$ 2.60	–	44.60 $\pm$ 4.10	2.379 $\pm$ 0.132	–	(Zapata <i>et al.</i> , 2020; Valencia Zapata <i>et al.</i> , 2019; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA	110.33 $\pm$ 1.25	0.958 $\pm$ 0.106	64.20 $\pm$ 2.70	2.764 $\pm$ 0.578	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-20 wt% CS	112.43 $\pm$ 1.27	1.259 $\pm$ 0.279	68.50 $\pm$ 0.70	3.398 $\pm$ 0.633	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-20 wt% (CS /MWCNTs)	118.71 $\pm$ 1.24	1.406 $\pm$ 0.130	78.50 $\pm$ 1.65	4.770 $\pm$ 0.290	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-25 wt% CS	113.67 $\pm$ 1.88	1.393 $\pm$ 0.253	71.63 $\pm$ 2.75	3.688 $\pm$ 0.939	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-25 wt% (CS /MWCNTs)	127.33 $\pm$ 7.41	1.675 $\pm$ 0.175	107.80 $\pm$ 2.30	5.706 $\pm$ 0.527	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020a,c)
PMMA-30 wt% CS	116.67 $\pm$ 1.69	1.166 $\pm$ 0.166	76.63 $\pm$ 3.72	4.276 $\pm$ 0.081	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA-30 wt% (CS /MWCNTs)	120.51 $\pm$ 1.40	1.277 $\pm$ 0.087	86.70 $\pm$ 3.10	5.343 $\pm$ 0.228	–	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020c)
PMMA	80.00 $\pm$ 2.10	0.719 $\pm$ 0.018	64.40 $\pm$ 2.70	–	–	(Tavakoli <i>et al.</i> , 2020a)
PMMA-20 wt% CS	81.20 $\pm$ 3.60	0.893 $\pm$ 0.121	69.50 $\pm$ 1.10	–	–	(Tavakoli <i>et al.</i> , 2020a)
PMMA-20 wt% (CS/GO)	86.00 $\pm$ 0.00	1.044 $\pm$ 0.028	75.20 $\pm$ 0.90	–	–	(Tavakoli <i>et al.</i> , 2020a)
PMMA-25 wt% CS	87.60 $\pm$ 1.20	0.974 $\pm$ 0.175	71.60 $\pm$ 1.40	–	–	(Tavakoli <i>et al.</i> , 2020a)
PMMA-25 wt% (CS/GO)	93.00 $\pm$ 4.00	1.217 $\pm$ 0.083	79.90 $\pm$ 1.80	–	–	(Tavakoli <i>et al.</i> , 2020a; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA-30 wt% CS	84.30 $\pm$ 2.00	0.936 $\pm$ 0.055	62.60 $\pm$ 1.10	–	–	(Tavakoli <i>et al.</i> , 2020a)
PMMA-30 wt% (CS/GO)	88.60 $\pm$ 1.60	1.106 $\pm$ 0.098	76.10 $\pm$ 1.30	–	–	(Tavakoli <i>et al.</i> , 2020a)
PMMA	90.60 $\pm$ 0.70	1.163 $\pm$ 0.073	38.00 $\pm$ 5.70	0.628 $\pm$ 0.048	–	(Lin <i>et al.</i> , 2005)
PMMA/50 wt% CS- β -TCP (Electrostatic system)	44.30 $\pm$ 16.70	0.779 $\pm$ 0.221	6.10 $\pm$ 1.10	0.130 $\pm$ 0.023	–	(Lin <i>et al.</i> , 2005)
PMMA/66.7 wt% CS- β -TCP(Electrostatic system)	14.60 $\pm$ 5.50	0.419 $\pm$ 0.029	8.10 $\pm$ 1.50	0.155 $\pm$ 0.029	–	(Lin <i>et al.</i> , 2005)

(Continued)

Table 2 Continued

Sample of BCs	Compressive strength (MPa)	Compressive modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Fracture toughness (K_{IC}) (MPa m ^{1/2})	Reference
PMMA/50 wt% CS- β -TCP (Emulsion technique)	83.50 $\pm$ 0.30	1.099 $\pm$ 0.179	23.00 $\pm$ 1.40	0.555 $\pm$ 0.015	–	(Lin <i>et al.</i> , 2005)
PMMA/66.7 wt% CS- β -TCP(Emulsion technique)	73.50 $\pm$ 1.40	1.136 $\pm$ 0.024	22.50 $\pm$ 0.70	0.558 $\pm$ 0.012	–	(Lin <i>et al.</i> , 2005)
PMMA/SiO ₂	98.30 $\pm$ 1.10	–	41.50 $\pm$ 1.50	–	–	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /50 wt% TCP	88.10 $\pm$ 1.90	–	32.40 $\pm$ 2.00	–	–	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /15 wt% HEMA	102.00 $\pm$ 1.40	–	46.80 $\pm$ 1.80	–	–	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /15 wt% HEMA/0.6 wt% EGDMA	103.60 $\pm$ 1.30	–	49.20 $\pm$ 1.80	–	–	(Yang <i>et al.</i> , 1997)
PMMA/SiO ₂ /50 wt% TCP/15 wt% HEMA/0.6 wt% EGDMA	91.20 $\pm$ 1.10	–	34.40 $\pm$ 1.50	–	–	(Yang <i>et al.</i> , 1997)
PMMA (Before soaking in SBF)	$\approx$ 76	–	–	–	–	(Tsukeoka <i>et al.</i> , 2006)
Modified PMMA(Before soaking in SBF)	$\approx$ 77	–	–	–	–	(Tsukeoka <i>et al.</i> , 2006)
PMMA (After soaking in SBF for 7 days)	$\approx$ 90	–	–	–	–	(Tsukeoka <i>et al.</i> , 2006)
Modified PMMA (After soaking in SBF for 7 days)	$\approx$ 60	–	–	–	–	(Tsukeoka <i>et al.</i> , 2006)
PMMA	127.40 $\pm$ 16.80	$\approx$ 1.30	–	–	–	(Fang <i>et al.</i> , 2019)
PMMA/16.25 wt% TCP/8.75 wt% CS	109.00 $\pm$ 0.60	$\approx$ 1.20	–	–	–	(Fang <i>et al.</i> , 2019)
PMMA/21.71 wt% TCP/11.69 wt% CS	107.50 $\pm$ 4.90	$\approx$ 1.19	–	–	–	(Fang <i>et al.</i> , 2019)
PMMA/32.5 wt% TCP/17.5 wt% CS	108.80 $\pm$ 3.50	$\approx$ 1.10	–	–	–	(Fang <i>et al.</i> , 2019)
PMMA/43.29 wt% TCP/23.31 wt% CS	90.30 $\pm$ 6.70	$\approx$ 1.05	–	–	–	(Fang <i>et al.</i> , 2019)
PMMA/48.75 wt% TCP/26.25 wt% CS	72.10 $\pm$ 6.20	$\approx$ 1.00	–	–	–	(Fang <i>et al.</i> , 2019)
PMMA	124.44 $\pm$ 8.50	1.153 $\pm$ 0.032	–	–	–	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL	100.04 $\pm$ 7.00	0.406 $\pm$ 0.008	–	–	–	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL/20 wt% BAGH	108.51 $\pm$ 7.30	0.851 $\pm$ 0.029	–	–	–	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL/40 wt% BAGH	101.80 $\pm$ 4.40	0.801 $\pm$ 0.021	–	–	–	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA-PCL/60 wt% BAGH	70.06 $\pm$ 4.20	0.796 $\pm$ 0.022	–	–	–	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA	$\approx$ 70	$\approx$ 3.50	–	–	–	(Sun <i>et al.</i> , 2019)
PMMA/10 wt% Calcium Silicate	$\approx$ 73	$\approx$ 3.25	–	–	–	(Sun <i>et al.</i> , 2019)
PMMA/20 wt% Calcium Silicate	$\approx$ 70	$\approx$ 3.00	–	–	–	(Sun <i>et al.</i> , 2019)
PMMA/30 wt% Calcium Silicate	$\approx$ 74	$\approx$ 3.00	–	–	–	(Sun <i>et al.</i> , 2019)
PMMA/40 wt% Calcium Silicate	$\approx$ 73	$\approx$ 2.26	–	–	–	(Sun <i>et al.</i> , 2019)
PMMA	90.53 $\pm$ 4.39	1.91 $\pm$ 0.08	–	–	–	(Li <i>et al.</i> , 2015)
PMMA/5 wt% MC	90.10 $\pm$ 2.90	1.84 $\pm$ 0.09	–	–	–	(Li <i>et al.</i> , 2015)
PMMA/10 wt% MC	90.16 $\pm$ 2.00	1.52 $\pm$ 0.09	–	–	–	(Li <i>et al.</i> , 2015)
PMMA/15 wt% MC	89.30 $\pm$ 5.26	1.21 $\pm$ 0.12	–	–	–	(Li <i>et al.</i> , 2015)
PMMA/20 wt% MC	88.03 $\pm$ 4.74	1.63 $\pm$ 0.07	–	–	–	(Li <i>et al.</i> , 2015)

Table 2 Continued

Sample of BCs	Compressive strength (MPa)	Compressive modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Fracture toughness (K_{IC}) (MPa m ^{1/2})	Reference
PMMA	107.20 ± 11.40	—	61.60 ± 10.20	3.067 ± 0.456	1.53 ± 0.13	(Paz <i>et al.</i> , 2017)
PMMA/0.1 wt% G	95.70 ± 12.80	—	48.30 ± 7.90	2.462 ± 0.535	1.95 ± 0.24	(Paz <i>et al.</i> , 2017)
PMMA/0.25 wt% G	98.80 ± 11.40	—	50.60 ± 9.60	2.204 ± 0.098	1.64 ± 0.24	(Paz <i>et al.</i> , 2017)
PMMA/0.5 wt% G	98.90 ± 15.20	—	52.40 ± 11.90	2.510 ± 0.452	1.63 ± 0.22	(Paz <i>et al.</i> , 2017)
PMMA/1.0 wt% G	97.70 ± 9.70	—	46.60 ± 7.10	2.278 ± 0.311	1.51 ± 0.23	(Paz <i>et al.</i> , 2017)
PMMA/0.1 wt% GO	120.70 ± 16.10	—	66.40 ± 6.50	3.293 ± 0.143	2.17 ± 0.11	(Paz <i>et al.</i> , 2017; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA/0.25 wt% GO	106.30 ± 19.30	—	69.80 ± 8.90	3.375 ± 0.169	2.08 ± 0.13	(Paz <i>et al.</i> , 2017)
PMMA/0.5 wt% GO	116.20 ± 9.10	—	63.80 ± 6.00	3.226 ± 0.098	2.04 ± 0.14	(Paz <i>et al.</i> , 2017)
PMMA/1.0 wt% GO	103.30 ± 19.10	—	61.60 ± 10.20	3.084 ± 0.128	1.64 ± 0.44	(Paz <i>et al.</i> , 2017)
PMMA/PCL	79.00 ± 5.60	0.391 ± 0.008	—	—	—	(Pahlevanzadeh <i>et al.</i> , 2018)
PMMA/PCL/FA	83.20 ± 6.00	0.80 ± 0.025	—	—	—	(Pahlevanzadeh <i>et al.</i> , 2018)
PMMA/PCL/GO	84.60 ± 5.50	0.40 ± 0.007	—	—	—	(Pahlevanzadeh <i>et al.</i> , 2018)
PMMA-PCL/FA/GO	101.80 ± 5.80	0.502 ± 0.01	—	—	—	(Pahlevanzadeh <i>et al.</i> , 2018; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA	30	—	—	—	—	(Phakatkar <i>et al.</i> , 2020)
PMMA-10 wt% MgP nanosheet	49	—	—	—	—	(Phakatkar <i>et al.</i> , 2020)
PMMA/10 wt% HA nanofiber	38	—	—	—	—	(Phakatkar <i>et al.</i> , 2020)
PMMA-7.5 wt% MgP nanosheet/2.5 wt% HA nanofiber	58	—	—	—	—	(Phakatkar <i>et al.</i> , 2020)
PMMA-5 wt% MgP nanosheet/5 wt% HA nanofiber	56	—	—	—	—	(Phakatkar <i>et al.</i> , 2020)
PMMA-2.5 wt% MgP nanosheet/7.5 wt% HA nanofiber	52	—	—	—	—	(Phakatkar <i>et al.</i> , 2020)
PMMA	87.90 ± 2.70	—	59.40 ± 7.80	1.56 ± 0.28	—	(Goto <i>et al.</i> , 2005)
PMMA/50 wt% TiO ₂	70.30 ± 9.70	—	34.40 ± 4.50	2.80 ± 0.70	—	(Goto <i>et al.</i> , 2005)
PMMA/50 wt% silanized TiO ₂	91.80 ± 7.70	—	25.50 ± 9.50	2.37 ± 0.63	—	(Goto <i>et al.</i> , 2005)
PMMA/60 wt% silanized TiO ₂	89.20 ± 10.60	—	27.50 ± 5.70	2.24 ± 0.62	—	(Goto <i>et al.</i> , 2005)
PMMA	85.90 ± 2.10	1.732 ± 0.070	56.30 ± 0.70	2.213 ± 0.054	2.03 ± 0.08	(Slane <i>et al.</i> , 2014)
PMMA/0.5 wt% MSNs	88.50 ± 2.40	1.776 ± 0.059	56.30 ± 1.30	2.475 ± 0.051	1.50 ± 0.16	(Slane <i>et al.</i> , 2014)
PMMA/2 wt% MSNs	85.70 ± 2.30	1.788 ± 0.052	50.70 ± 0.60	2.398 ± 0.042	1.12 ± 0.10	(Slane <i>et al.</i> , 2014)
PMMA/5 wt% MSNs	89.50 ± 2.60	1.883 ± 0.051	47.00 ± 1.40	2.564 ± 0.048	0.86 ± 0.13	(Slane <i>et al.</i> , 2014)
PMMA	≈ 80	≈ 1.23	—	—	—	(Russo <i>et al.</i> , 2017)
PMMA/0.25 wt% AuNPs	≈ 90	≈ 1.32	—	—	—	(Russo <i>et al.</i> , 2017)
PMMA/0.5 wt% AuNPs	≈ 76	≈ 1.33	—	—	—	(Russo <i>et al.</i> , 2017)
PMMA/1 wt% AuNPs	≈ 75	≈ 1.40	—	—	—	(Russo <i>et al.</i> , 2017)
PMMA (Before soaking in SBF)	≈ 90	≈ 0.57	—	—	—	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (9:1 vol%) (Before soaking in SBF)	≈ 62	≈ 0.42	—	—	—	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (8:2 vol%) (Before soaking in SBF)	≈ 54	≈ 0.33	—	—	—	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (7:3 vol%) (Before soaking in SBF)	≈ 50	≈ 0.28	—	—	—	(Tang <i>et al.</i> , 2017)

(Continued)

Table 2 Continued

Sample of BCs	Compressive strength (MPa)	Compressive modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)	Fracture toughness (K_{IC}) (MPa m ^{1/2})	Reference
PMMA (After soaking in SBF for 4 h)	≈ 90	≈ 0.54	–	–	–	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (9:1 vol%) (After soaking in SBF for 4 h)	≈ 58	≈ 0.33	–	–	–	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (8:2 vol%) (After soaking in SBF for 4 h)	≈ 35	≈ 0.25	–	–	–	(Tang <i>et al.</i> , 2017)
PMMA/PAAS _f (7:3 vol%) (After soaking in SBF for 4 h)	≈ 24	≈ 0.19	–	–	–	(Tang <i>et al.</i> , 2017)

permitted by the standard. However for the BC that contained both CS and GO, bending strength was not significantly different with respect to reference BC. Alternatively, the encapsulation of GO into BCs did not cause any significant enhancement in mechanical performance in comparison with the BCs reference specimen (Zapata *et al.*, 2020). In another study by Soleymani Eil Bakhtiari *et al.* (2020c) adding 25 wt% CS/MWCNTs composite powder to the PMMA-based BCs significantly increased the compressive and bending strength (Soleymani Eil Bakhtiari *et al.*, 2020a,c). Furthermore, in another study by Tavakoli *et al.* (2020a) adding 25 wt% of CS/GO composite powder to the PMMA-based BCs also increased the compressive strength by 16.2%, the compressive modulus by 69.1%, and the bending strength by 24.0% (Tavakoli *et al.*, 2020a; Soleymani Eil Bakhtiari *et al.*, 2020a). In another study (Lin *et al.*, 2005), the UCS and bending strength were decreased due to the presence of CS/ β -TCP microspheres in PMMA-based BCs (Lin *et al.*, 2005). Moreover, in another study by Yang *et al.* (1997) adding TCP to PMMA/SiO₂-based BCs caused to decrease in compressive and bending strengths, but the addition of HEMA and EGDMA in the new BCs had the opposite effect of TCP (Yang *et al.*, 1997). As for modified PMMA-based BCs (Tsukeoka *et al.*, 2006), the modified BCs without soaking in simulated body fluid (SBF) had almost the same compressive strength as the conventional ones, but soaking in SBF decreased the strength unlike the value recommended by ISO5833 (70 MPa). The compressive strength of the Modified BCs is possibly diminished by calcium acetate and section of the hydrolyzed MPS (Tsukeoka *et al.*, 2006). In another study conducted on the PMMA-TCP/CS-based BCs by Fang *et al.* (2019), adding TCP and CS into the pure PMMA-based BC led to decreased compressive Young's modulus and UCS in comparison with the pure PMMA-based BC (Fang *et al.*, 2019). In another study by Pahlevanzadeh *et al.* (2019b) incorporating 20 and 40 wt% BAGH into the PMMA/PCL-based BCs increased the compressive strength and elastic modulus of the BCs (Pahlevanzadeh *et al.*, 2019b). In the study by Sun *et al.* (2019), bioactive injectable PMMA/calcium silicate-based BCs were prepared for percutaneous vertebroplasty and kyphoplasty. Obtained results indicated that PMMA/calcium silicate hybrid BCs sufficiently retained the mechanical strength in comparison with the pure PMMA-based BC, but obtained results from Young's modulus indicated that by adding calcium silicate into the PMMA-based BC, lower Young's modulus achieved (Sun *et al.*, 2019). In another study (Li *et al.*, 2015), the mechanical properties of PMMA/MC-based BCs revealed that the presence of 15 wt% impregnated PMMA-MC significantly decreased compressive modulus, although a little effect on compressive strength and solidification (Li *et al.*, 2015). In other study by Wekwejt *et al.* (2020), the compressive strength evaluation of PMMA-based BCs revealed that the encapsulation of Mg and TCP failed to impact the compressive strength of the BCs; although CS, cellulose, and PDO decreased substantially compressive strength of PMMA-based BCs by 13%, 17% and 24%, respectively (Wekwejt *et al.*, 2020). In another study by (Paz *et al.*, 2017), it was reported that the mechanical behavior of PMMA/G and PMMA/GO-based BCs had been enhanced at low loadings of (≤ 0.25 wt%) due to G and GO-induced deflection in fronts of the crack, which can inhibit the crack from propagation (Paz *et al.*, 2017). Compared to G, the modified GO led to greater improvements considering that it enabled the development of greater interfacial attachment among the GO and PMMA. As a result of the emerging of agglomerates and escalating the amount of porosity via incorporation of more than 0.25 wt% GO, the mechanical characteristics could be reduced (Paz *et al.*, 2017). The obtained results of PMMA-PCL/FA/GO-based BCs (Pahlevanzadeh *et al.*, 2018) showed that adding GO to PMMA-PCL/FA-based BCs enhances the mechanical properties due to a high amount of functional groups, including hydroxyl and carboxyl on the surface of GO. Moreover, the GO sheets have a large specific surface area besides its wrinkly surface, leading to a higher adhesion/interlock between GO and the polymer-based matrix (Pahlevanzadeh *et al.*, 2018; Gonçalves *et al.*, 2012; Soleymani Eil Bakhtiari *et al.*, 2020a). In another study by Phakatkar *et al.* (2020) that conducted on PMMA-Mg/HA-based BCs, the incorporation of both fillers can lock the deformation, thus enhancing the compressive strength of the nanocomposites. The findings consequently exhibited that the PMMA nanocomposite containing 7.5 wt% MgP nanosheets and 2.5 wt% HA nanofibers presented great compressive strength. Nevertheless, by escalating the amount of HA nanofibers from 5 to 7.5 wt% in the PMMA composite BC, the compressive strength diminished progressively. It appears that escalating the amount of HA nanofibers more than 2.5 wt% could possibly cause to the agglomeration hence decreasing the homogeneity of BC composite matrix that can eventually decrease the compressive strength by helping the

formation of voids and internal cavities (Phakatkar *et al.*, 2020; Singh *et al.*, 2008). In another study by Goto *et al.* (2005), bioactive PMMA-based BCs containing nTiO₂ particles were fabricated for use as bone substitutes. The results obtained from PMMA/silanized TiO₂-based BCs showed that adding 60 wt% silanized TiO₂ to PMMA-based BCs provides an equivalent compressive strength (Goto *et al.*, 2005). In other study by Slane *et al.* (2014), PMMA-based BCs were modified with MSNs and their mechanical, fatigue and absorption properties were investigated. In this perspective, Slane *et al.* (2014) depicted that greater MSNs amount leads to enhancement of the mechanical characteristics (flexural modulus, compressive strength and modulus). On the other hand, the flexural strength and fracture toughness diminished drastically with the escalating MSNs amount. MSNs strongly affected the fatigue characteristics, with significant detrimental effects when a high MSN amount was incorporated in the BC. These findings point out that MSN as used in this study, was not an efficient reinforcement phase utilizing in PMMA-based BC (Slane *et al.*, 2014). Russo *et al.* (2017) examined the mechanical characteristic of PMMA-based BCs encapsulated with AuNPs. Their finding demonstrated that the addition of AuNPs amplified the compressive modulus of BCs slightly. Especially by introducing 1 wt% of AuNPs, the compressive modulus for the nanocomposite BC was higher in comparison with that pure BC and other BC formulations. Their result likewise depicted that the addition of 0.25 wt% of AuNPs, on the other hand, appeared to improve the maximum stress of the BC, although a reduction was noticed by more escalating the amount of AuNPs. It was worth noting that less significant variations were observed between pure BC and nanocomposite BCs (Russo *et al.*, 2017). Before and after SBF incubation for 4 h, the compressive strengths of PMMA/PAAS_f-based BCs were assessed by Tang *et al.* (2017). The compressive strength of pure PMMA-based BC was around 90 MPa. The pure PMMA-based BC was not degraded in the SBF; consequently, the compressive strength stayed predominately unaffected after incubation in SBF. By escalating PAAS_f amount, the compressive strengths of PMMA/PAAS_f-based BCs prior to incubation in SBF diminished slowly because the strength of PAAS_f was lower compared with PMMA. Furthermore, in contrast to those prior to incubation, absorption of SBF and the expansion of the volume of the BCs containing PAAS_f after incubation in SBF for 4 h get through to saturation level, and the compressive strength of BCs diminished (Tang *et al.*, 2017). After incubation in SBF, the three-dimensional structure of PAAS_f shaped a hydrogel with a substantial water amount (Xue *et al.*, 2014). In this view, Tang *et al.* (2017) also indicated that with volume expansion of the BCs; the compressive strength of the BCs containing PAAS_f were significantly decreased (Tang *et al.*, 2017).

Effect of Different Reinforcements on Biological Properties

As mentioned above, traditional acrylic BCs could not regularly increase bone ingrowth. In order to enhance the biological behavior of the BCs, they should contain various types of reinforcements. The cellular response of PMMA-based BCs containing different reinforcements including HA, HA/CS, MWCNTs, CS, quaternized CS, CS/GO, CS/MWCNTs, TCP/CS, PCL/BAGH, calcium silicate, MC, PCL/FA/GO, MgP, silanized TiO₂, nano MgO, nano BaSO₄ and PAAS_f are tabulated in Table 3.

HA is one of the reinforcements that used in order to improve biological properties of PMMA-based BCs. In studies (Dalby *et al.*, 1999, 2001) adding HA to the PMMA-based BCs provide a more appropriate substrate for human osteoblast (HOB) cells, leading to an increase in cell proliferation and alkaline phosphatase (ALP) activity (Dalby *et al.*, 1999, 2001; Soleymani Eil Bakhtiari *et al.*, 2020b). In another study by Pino-Mínguez *et al.* (2015), biological results from PMMA/HA-based BCs indicated that at a concentration between 15% and 20% provided a favored condition for osteoblastic proliferation without altering their osteogenic capacity and lower toxicity than pure PMMA and composites with lower concentrations (Pino-Mínguez *et al.*, 2015). In other studies (Itokawa *et al.*, 2007; Sa *et al.*, 2017) PMMA/HA-based BCs were regarded as good candidates for cranial bone implants due to its good osteoconduction and biocompatibility (Itokawa *et al.*, 2007; Sa *et al.*, 2017). In another study (Kim *et al.*, 2004), the results of *in vitro* and animal studies of the PMMA-HA/CS-based BCs indicated that the proposed BCs have the potential for clinical applications as replacements for the pure commercial PMMA-based BCs (Kim *et al.*, 2004). In another study by Wang *et al.* (2019), *in vitro* study of PMMA/MWCNTs-based BCs represented that adding MWCNTs to the PMMA-based BCs improved cell adhesion and proliferation. Moreover, *in vivo* study indicated that new bone formation inside the BCs and the integration between the BCs and bone tissue were significantly enhanced with an increase in MWCNTs content within 12 weeks of post-surgery (Wang *et al.*, 2019; Soleymani Eil Bakhtiari *et al.*, 2020a,b). In another study by Ormsby *et al.* (2012), the obtained results of PMMA/MWCNTs-based BCs showed that adding MWCNTs to the PMMA-based BCs, caused to a better attachment and proliferation of MG-63 osteoblastic cells on the BCs (Ormsby *et al.*, 2012; Soleymani Eil Bakhtiari *et al.*, 2020a,b). In another study by Endogan *et al.* (2014), *in vivo* studies performed on PMMA/CS-based BCs confirmed appropriate bone-bonding ability and bioactivity of them (Endogan *et al.*, 2014). In other study by Tan *et al.* (2012), the cellular behavior of PMMA/quaternized CS-based BCs presented a higher stem cell proliferation, osteogenic differentiation, and osteogenesis-associated genes expression on their surfaces in comparison with the gentamicin-loaded PMMA-based BCs (Tan *et al.*, 2012). In another study by Valencia Zapata *et al.* (2019) the presence of CS and GO improved ALP activity in the PMMA-CS/GO-based BCs (Valencia Zapata *et al.*, 2019). In another study by Zapata *et al.* (2020) cell viability and cell attachment of PMMA-CS/GO-based BC examined, and their findings revealed that BC presents great cell response. In their *in vivo* study, both subdermal and bone parietal implantations in Wistar rats were evaluated. Modified PMMA-based BCs revealed a lack of immune reaction, as verified by a normal inflammatory response in Wistar rat subdermal implantation. The outcomes of the parietal bone implantation proved that the incorporation of CS and GO together permitted a near-complete healing bone-cement interface, as detected in the micrographic examination (Zapata *et al.*, 2020). In another study by Soleymani Eil Bakhtiari *et al.* (2020c) by adding 25 wt% CS/MWCNTs composite powder to PMMA-based BC, the activity of the osteocyte cells leads to the formation of the extracellular matrix (ECM), leading to an increase in the

Table 3 Cellular responses of PMMA-based composite BCs containing different types of reinforcements

Sample of BCs	Cellular assay	Cell type	Target tissue	Application	Reference
PMMA/17.5 wt% HA	Increasing in proliferation and ALP activity	Primary human osteoblast (HOB)-like cells	Bone	<i>In vitro</i>	(Dalby <i>et al.</i> , 1999; Soleymani Eil Bakhtiari <i>et al.</i> , 2020b)
PMMA/17.5 wt% HA	Increasing in expression of adhesion plaques, Higher cell proliferation and differentiation, Higher levels of ALP activity	Primary human osteoblast (HOB)-like cells	Bone	<i>In vitro</i>	(Dalby <i>et al.</i> , 2001)
PMMA/15 and 20 wt% HA	Better osteoblast response, with higher osteoblastic activity markers, Lower apoptosis markers	Human osteoblasts (cellular lineage ATTC Saos-2)	Bone	<i>In vitro</i>	(Pino-Minguez <i>et al.</i> , 2015)
PMMA/67 wt% HA	Good osteoconductivity and biocompatibility	—	Bone	<i>In vivo</i>	(Itokawa <i>et al.</i> , 2007)
PMMA/HA	Good osteoconductivity, Supporting direct bone-to cement contact	—	Bone	<i>In vivo</i>	(Sa <i>et al.</i> , 2017)
PMMA-50 wt% HA/10 wt% CS	Improvement in cell attachment and proliferation	Human osteoblast (HOB)-like cells, MG-63	Bone	<i>In vitro</i>	(Kim <i>et al.</i> , 2004)
PMMA-50 wt% HA/10 wt% CS	More biocompatible and osteoconductive than pure PMMA-based BC	—	Bone	<i>In vivo</i>	(Kim <i>et al.</i> , 2004)
PMMA/MWCNTs	Improvement in cell adhesion and proliferation. Promotion in osteogenic differentiation	Rat bone marrow-derived mesenchymal stem cells (rBMSCs)	Bone	<i>In vitro</i>	(Wang <i>et al.</i> , 2019; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a,b)
PMMA/MWCNTs	New bone formation, Significant enhancement in the integration between the BC and bone tissue	—	Bone	<i>In vivo</i>	(Wang <i>et al.</i> , 2019)
PMMA/MWCNTs	Successfully adherence and proliferation on the surfaces of all PMMA/MWCNTs-based BCs	Osteoblast-like MG-63 cells	Bone	<i>In vitro</i>	(Ormsby <i>et al.</i> , 2012; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a,b)
PMMA/CS (0.05 g/g) (Particle size range of PMMA: 50–150 μ m)	Enhancement in <i>in vivo</i> osteogenic activity	—	Bone	<i>In vivo</i>	(Endogan <i>et al.</i> , 2014)
PMMA/Quaternized CS	Improvement in stem cell proliferation, Osteogenic differentiation, Expressing osteogenesis-associated genes on the surface of the BCs	Human mesenchymal stem cells (hMSCs)	Bone	<i>In vitro</i>	(Tan <i>et al.</i> , 2012)
PMMA-15 wt% CS and 0.3 wt% GO/15 wt% CS	Enhancing ALP activity, Inducing osteoblastic activity, Increasing osteogenic activity, Supporting good cell viability of HOB	Human osteoblasts (HOB)	Bone	<i>In vitro</i>	(Valencia Zapata <i>et al.</i> , 2019)
PMMA-0.3 wt%GO/15 wt% CS	Higher extracellular matrix (ECM) formation	Human osteoblasts (HOB) cells (ECACC 06090739)	Bone	<i>In vitro</i>	(Zapata <i>et al.</i> , 2020)
PMMA-0.3 wt%GO/15 wt% CS	Enhancement in biomineralization, Greater integration with bone, Improvement in biocompatibility	—	Bone	<i>In vivo</i> (subdermal and bone parietal implantations)	(Zapata <i>et al.</i> , 2020)
PMMA-25 wt% (CS/MWCNTs)	The activity of the osteocyte cells led to the formation of the ECM	Human osteosarcoma cell line MG-63	Bone	<i>In vitro</i>	(Soleymani Eil Bakhtiari <i>et al.</i> , 2020 a,b,c)
PMMA-25 wt% (CS/GO)	Improvement in cell viability, growth, and cell adhesion	Osteoblast-like cell line (MG-63)	Bone	<i>In vitro</i>	(Tavakoli <i>et al.</i> , 2020a; Soleymani Eil Bakhtiari <i>et al.</i> , 2020 a,b)
PMMA/TCP/CS	Non-cytotoxic	Mouse fibroblast cell line (L929)	Bone	<i>In vitro</i>	(Fang <i>et al.</i> , 2019)
PMMA/TCP/CS	More osteoconductivity	—	Bone	<i>In vivo</i>	(Fang <i>et al.</i> , 2019)
PMMA-PCL/BAGH	Improvement in the viability of MG-63 osteoblasts, Higher cell attachment and spreading	MG-63	Bone	<i>In vitro</i>	(Pahlevanzadeh <i>et al.</i> , 2019b)
PMMA/Calcium Silicate	Well grow ability,Excellent proliferation viability	Human bone marrow stromal cells (HBMSCs)	Bone	<i>In vitro</i>	(Sun <i>et al.</i> , 2019)
PMMA/Calcium Silicate	Remarkable degradation, Significant new bone formation	—	—	<i>In vivo</i>	(Sun <i>et al.</i> , 2019)

Table 3 Continued

Sample of BCs	Cellular assay	Cell type	Target tissue	Application	Reference
PMMA/MC	Excellent bone tissue compatibility	L929 mouse connective tissue cells	Bone	<i>In vitro</i>	(Li <i>et al.</i> , 2015)
PMMA/MC	Higher bone-cement interface crosslinking than control BC after 6 months implantation in the femur of rabbits.	–	Bone	<i>In vivo</i>	(Li <i>et al.</i> , 2015)
PMMA-PCL/FA/GO	High cells viability	MG-63 osteoblast cells	Bone	<i>In vitro</i>	(Pahlevanzadeh <i>et al.</i> , 2018; Soleymani Eil Bakhtiari <i>et al.</i> , 2020a)
PMMA/10 wt% HA nanofiber	More cells survived than other BCs	Fibroblasts cells	Bone	<i>In vitro</i>	(Phakatkar <i>et al.</i> , 2020)
PMMA-10 wt% MgP nanosheet	Highest amount of cytocompatibility	Fibroblasts cells	Bone	<i>In vitro</i>	(Phakatkar <i>et al.</i> , 2020)
PMMA/60 wt% silanized TiO ₂	Better osteoconductivity than other BCs	–	Bone	<i>In vivo</i>	(Goto <i>et al.</i> , 2005)
PMMA/nano MgO	Enhancement in osteoblast adhesion	Human osteoblasts (CRL-11372)	Bone	<i>In vitro</i>	(Ricker <i>et al.</i> , 2008)
PMMA/nano BaSO ₄	Enhancement in osteoblast adhesion	Human osteoblasts (CRL-11372)	Bone	<i>In vitro</i>	(Ricker <i>et al.</i> , 2008)
PMMA/MC	Cells can start proliferation and differentiation earlier a few days on PMMA/MC-based BCs than that on PMMA-based BC	Human bone marrow-derived stem cells	Bone	<i>In vitro</i>	(Wu <i>et al.</i> , 2016)
PMMA/PAAS ₁	No significant difference existed between composite BCs and PMMA-based BC in cytotoxicity test	Fibroblast cells	Bone	<i>In vitro</i>	(Tang <i>et al.</i> , 2017)

possibility of cellular differentiation (Soleymani Eil Bakhtiari *et al.*, 2020a,b,c). In another study by Tavakoli *et al.* (2020a) the results obtained from the cell culture study of MG-63 confirmed the improvement of cell viability, growth, and cell attachment on the 25 wt% of PMMA-CS/GO-based composite BC (Tavakoli *et al.*, 2020a; Soleymani Eil Bakhtiari *et al.*, 2020a,b). In another study (Fang *et al.*, 2019), cell proliferation tests of the PMMA-TCP/CS-based BCs confirmed the non-cytotoxicity of them. Moreover, *in vivo* studies revealed that they are more osteoconductive than pure PMMA-based BC (Fang *et al.*, 2019). In another study by Pahlevanzadeh *et al.* (2019b) 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium-bromide (MTT) assay demonstrated an enhanced cellular activity of the BC in combination with BAGH. The osteoblast adhesion and spreading ability on the BC containing BAGH were significantly higher than the BC without BAGH in the same duration of cell culture, and ALP activity on the BC containing BAGH was also higher than the BC without BAGH on the 3rd and 7th days (Pahlevanzadeh *et al.*, 2019b). In another study by (Sun *et al.*, 2019) *in vitro* study of the PMMA/calcium silicate hybrid BCs revealed that human bone marrow stromal cells (HBMSCs) were able to grow well while presented excellent cell proliferation and viability. Moreover, *in vivo* study in goat vertebral body defect models demonstrated well biodegradability and significant promotion of new bone formation in defects within 6 months of post-injection (Sun *et al.*, 2019). In this perspective, Wekwejt *et al.* (2020) disclose that reinforced BCs with cellulose, CS, Mg, PDO, or TCP presented more apatite formation ability, which is connected with time-varying porosity. In turn, this impacts their osteoconductivity and plays a role in the effective release of active compounds that improve specimens' antibacterial efficacy. Additives, on the other hand, might decrease their cell viability, particularly at a greater concentration (Wekwejt *et al.*, 2020). In another study by Li *et al.* (2015) the biological properties of PMMA/MC-based BCs revealed that after adding MC to PMMA-based BCs, these BCs were biologically safe in cytotoxicity regarding blood compatibility, the local reaction after implantation, acute systemic toxicity, and chronic liver and kidney toxicity. Moreover, the BC interface crosslinking was significantly higher after implantation in the distal femur of rabbits. A comparison between gene expression of the PMMA/MC-based BCs and control PMMA-based BC groups also revealed that PMMA/MC-based BCs might improve osteogenic bioactivity (Li *et al.*, 2015). In other study by (Pahlevanzadeh *et al.*, 2018) the cytotoxicity test results related to the PMMA-PCL/FA/GO-based BCs represented that MG-63 osteoblast cell viability increased as the FA and GO contents added into the PMMA-PCL polymer BCs (Pahlevanzadeh *et al.*, 2018; Soleymani Eil Bakhtiari *et al.*, 2020a). In another study by Phakatkar *et al.* (2020) cellular obtained results from PMMA-MgP/HA-based BCs showed that the synthesized nanocomposite possesses excellent bioactivity and cytocompatibility potentially (Phakatkar *et al.*, 2020). In another study (Goto *et al.*, 2005), animal experiments of PMMA/60 wt% silanized TiO₂-based BC presented a significantly higher osteoconduction potential in comparison with the other BCs at each time interval (Goto *et al.*, 2005). In another study by Ricker *et al.* (2008) adding nanoparticles of MgO and BaSO₄ to PMMA-based BCs

led to an increase in osteoblast attachment on PMMA-based BCs (Ricker *et al.*, 2008). In another study conducted by Wu *et al.* (2016) adding MC to PMMA-based BCs indicated that osteogenic differentiation on MC incorporated in PMMA-based BCs was more than two times higher than PMMA-based BCs during 21 days of cell culture study (Wu *et al.*, 2016). In a study by Tang *et al.* (2017) cytotoxicity was compared between PMMA-based BC and PMMA/PAAS_F-based BCs, and their result indicated that their cytotoxicity did not differ considerably by the addition of PAAS_F (Tang *et al.*, 2017).

Conclusions and Future Work

PMMA, as a biocompatible polymer, has wide applications in medicine, especially in BCs. Because of some inappropriate properties of PMMA-based BCs such as thermogenesis during polymerization process, weak mechanical properties and lack of bioactivity, different methods developed to address these issues. Using ceramics, polymers, and composites as reinforcement agents in PMMA-based BCs is one of the common methods to enhance their physical, mechanical, and biological properties. Considering the reviewed studies on the BCs, using different reinforcement agents could create various advantages for PMMA-based BCs. Furthermore, interestingly, the addition of HA, GC, HA/CS, MWCNTs, *f*-MWCNTs, CS, quaternized CS, GO, CS/MWCNTs, CS/GO, CS- β -TCP, TCP, PCL/BAGH, cellulose, PDO, and PAAS_F into PMMA-based BCs have been proved to decrease maximum temperature and increase setting time. Moreover, the addition of HA in a smaller extent into PMMA/HA-based composite BCs increases mechanical properties since it acts as load-bearing. In particular, the superior mechanical properties of PMMA/carbon-based composite BCs can be attained with encapsulation of a specific amount of CBNs into the BC owing arresting/retarding crack propagation in the BCs structure for orthopedics applications. The studies have exhibited that BCs encapsulated with HA, CS, quaternized CS, CS/MWCNTs, PCL/BAGH, calcium silicate, PCL/FA/GO, HA nanofiber, MgP nanosheet, nano MgO, nano BaSO₄ are shown high cytocompatibility *in vitro*. In light of this, PMMA-based BCs containing HA/CS, CS/GO, TCP/CS, calcium silicate, MC, silanized TiO₂ induce bone formation *in vivo*. The continuous study progresses in PMMA-based BCs and is essential to the accomplishment of touchable and clinically pertinent outcomes in the treatment of bone defects.

References

- Aghyarian, S., Rodriguez, L.C., Chari, J., *et al.*, 2014. Characterization of a new composite PMMA-HA/Brushite bone cement for spinal augmentation. *Journal of Biomaterials Applications* 29 (5), 688–698.
- Ahmed, N., Khan, U., Mohyud-Din, S.T., 2020. Modified heat transfer flow model for SWCNTs-H₂O and MWCNTs-H₂O over a curved stretchable semi infinite region with thermal jump and velocity slip: A numerical simulation. *Physica A: Statistical Mechanics and its Applications* 545, 123431.
- Ayatollahi, M.R., Mirmohammadi, S.A., Shirazi, H.A., 2018. The tension-shear fracture behavior of polymeric bone cement modified with hydroxyapatite nano-particles. *Archives of Civil and Mechanical Engineering* 18, 50–59.
- Ayre, W.N., 2013. Novel approaches to the development of PMMA bone cement. A thesis submitted in partial fulfillment for the degree of Doctor of Philosophy.
- Breusch, S., Malchau, H., 2005. *The Well-Cemented Total Hip Arthroplasty: Theory and Practice*. Springer Medizin Verlag Heidelberg.
- Buchholz, H.W., 1970. Über die depotwirkung einiger antibiotika bei vermischung mit dem kunstharz palacos. *Chirurg* 40, 511–515.
- Cha, C., Shin, S.R., Annabi, N., Dokmeci, M.R., Khademhosseini, A., 2013. Carbon-based nanomaterials: Multifunctional materials for biomedical engineering. *ACS Nano* 7 (4), 2891–2897.
- Charnley, J., 1960. Anchorage of the femoral head prosthesis to the shaft of the femur. *The Journal of Bone and Joint Surgery: British Volume* 42 (1), 28–30.
- Charnley, J., 1970. Clinical experiences with self-curing acrylic cement. In *Acrylic Cement in Orthopaedic Surgery*. Edinburgh: E & S Livingstone, pp. 33–35.
- Chung, C., Kim, Y.K., Shin, D., *et al.*, 2013. Biomedical applications of graphene and graphene oxide. *Accounts of Chemical Research* 46 (10), 2211–2224.
- Compton, O.C., Nguyen, S.T., 2010. Graphene oxide, highly reduced graphene oxide, and graphene: Versatile building blocks for carbon-based materials. *Small* 6 (6), 711–723.
- Dalby, M.J., Di Silvio, L., Harper, E.J., Bonfield, W., 1999. *In vitro* evaluation of a new polymethylmethacrylate cement reinforced with hydroxyapatite. *Journal of Materials Science: Materials in Medicine* 10 (12), 793–796.
- Dalby, M.J., Di Silvio, L., Harper, E.J., Bonfield, W., 2001. Initial interaction of osteoblasts with the surface of a hydroxyapatite-poly (methylmethacrylate) cement. *Biomaterials* 22 (13), 1739–1747.
- Depan, D., Pesacreta, T.C., Misra, R.D., 2014. The synergistic effect of a hybrid graphene oxide–chitosan system and biomimetic mineralization on osteoblast functions. *Biomaterials Science* 2 (2), 264–274.
- Doi, Y., Nakatani, A., 2011. Structure and stability of nonlinear vibration mode in graphene sheet. *Procedia Engineering* 10, 3393–3398.
- Dunne, N., Clements, J., Wang, J.S., 2014. Acrylic cements for bone fixation in joint replacement. In *Joint Replacement Technology*. Woodhead Publishing, pp. 212–256.
- Dunne, N., Ormsby, R.W., 2011. MWCNT used in orthopaedic bone cements. In: Naraghi, M. (Ed.), *Carbon Nanotubes – Growth and Applications*. Tech Open Access Publisher, pp. 337–342.
- Dunne, N.J., Orr, J.F., 2002. Curing characteristics of acrylic bone cement. *Journal of Materials Science: Materials in Medicine* 13 (1), 17–22.
- Endogan, T., Kiziltay, A., Kose, G.T., *et al.*, 2014. Acrylic bone cements: Effects of the poly (methyl methacrylate) powder size and chitosan addition on their properties. *Journal of Applied Polymer Science* 131 (3).
- Fang, C.H., Lin, Y.W., Sun, J.S., Lin, F.H., 2019. The chitosan/tri-calcium phosphate bio-composite bone cement promotes better osteo-integration: An *in vitro* and *in vivo* study. *Journal of Orthopaedic Surgery and Research* 14 (1), 162.
- Ferreira, B.J., Barroca, N.B., Lopes, P.P., *et al.*, 2014. Properties of novel PMMA-co-EHA bone cements filled with hydroxyapatite. *Polymer Composites* 35 (4), 759–767.
- Gonçalves, G., Cruz, S.M.A., Ramalho, A., Grácio, J., Marques, P.A.A.P., 2012. Graphene oxide versus functionalized carbon nanotubes as a reinforcing agent in a PMMA/HA bone cement. *Nanoscale*, 4, 2937.
- Goto, K., Tamura, J., Shinzato, S., *et al.*, 2005. Bioactive bone cements containing nano-sized titania particles for use as bone substitutes. *Biomaterials*, 26 (33), 6496–6505.
- Haboush, E., 1953. A new operation for arthroplasty of the hip based on biomechanics, photoelasticity, fast-setting dental acrylic and other considerations. *Bulletin of the Hospital for Joint Diseases Orthopaedic Institute* 14, 242–277.
- Harakas, N.K., 1984. Demineralized bone-matrix-induced osteogenesis. *Clinical Orthopaedics and Related Research* 188, 239–251.

- Harper, E.J., Behiri, J.C., Bonfield, W., 1995. Flexural and fatigue properties of a bone cement based upon polyethylmethacrylate and hydroxyapatite. *Journal of Materials Science: Materials in Medicine* 6 (12), 799–803.
- Heikkilä, J.T., Aho, A.J., Kangasniemi, I., Yli-Urpo, A., 1996. Polymethylmethacrylate composites: Disturbed bone formation at the surface of bioactive glass and hydroxyapatite. *Biomaterials* 17, 1755–1760.
- Hendriks, J.G., Van Horn, J.R., Van Der Mei, H.C., Busscher, H.J., 2004. Backgrounds of antibiotic-loaded bone cement and prosthesis-related infection. *Biomaterials* 25 (3), 545–556.
- Hirlekar, R., Yamagar, M., Garse, H., Vij, M., Kadam, V., 2009. Carbon nanotubes and its applications: A review. *Asian Journal of Pharmaceutical and Clinical Research* 2 (4), 17–27.
- Huang, K.Y., Yan, J.J., Lin, R.M., 2005. Histopathologic findings of retrieved specimens of vertebroplasty with polymethylmethacrylate cement: Case control study. *Spine* 30 (19), E585–E588.
- Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature* 354 (6348), 56–58.
- Itokawa, H., Hiraide, T., Moriya, M., *et al.*, 2007. A 12 month in vivo study on the response of bone to a hydroxyapatite–polymethylmethacrylate cranioplasty composite. *Biomaterials* 28 (33), 4922–4927.
- Jaafari, K., Ruiz, T., Elmaleh, S., Coma, J., Benkhrouja, K., 2004. Simulation of a fixed bed adsorber packed with protonated cross-linked chitosan gel beads to remove nitrate from contaminated water. *Chemical Engineering Journal* 99 (2), 153–160.
- Jasty, M., Maloney, W.J., Bragdon, C.R., *et al.*, 1991. The initiation of failure in cemented femoral components of hip arthroplasties. *The Journal of Bone and Joint Surgery* 73, 551–558. British Volume.
- Jayakumar, R., Chennazhi, K.P., Srinivasan, S., *et al.*, 2011. Chitin scaffolds in tissue engineering. *International Journal of Molecular Sciences* 12 (3), 1876–1887.
- Jimenez, E.P., 2017. Bone cements reinforced with carbon based nanomaterials. PhD. Thesis.
- Judet, J., Judet, R., 1950. The use of an artificial femoral head for arthroplasty of the hip joint. *The Journal of Bone and Joint Surgery: British Volume* 32 (2), 166–173.
- Kalita, S.J., Bhardwaj, A., Bhatt, H.A., 2007. Nanocrystalline calcium phosphate ceramics in biomedical engineering. *Materials Science and Engineering: C* 27, 441–449.
- Khandaker, M., Meng, Z., 2015. The effect of nanoparticles and alternative monomer on the exothermic temperature of PMMA bone cement. *Procedia Engineering* 105, 946–952.
- Kim, S.B., Kim, Y.J., Yoon, T.L., *et al.*, 2004. The characteristics of a hydroxyapatite-chitosan-PMMA bone cement. *Biomaterials* 25 (26), 5715–5723.
- Kuehn, K.D., Ege, W., Gopp, U., 2005. Acrylic bone cements: Composition and properties. *Orthopedic Clinics* 36 (1), 17–28.
- Kumar, M.N., 2000. A review of chitin and chitosan applications. *Reactive and Functional Polymers* 46 (1), 1–27.
- Lam, C.W., James, J.T., McCluskey, R., Hunter, R.L., 2004. Pulmonary toxicity of single-wall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. *Toxicological Sciences* 77 (1), 126–134.
- Lee, R.R., Ogiso, M., Watanabe, A., Ishihara, K., 1997. Examination of hydroxyapatite filled 4-META/MMA-TBB adhesive bone cement in in vitro and in vivo environment. *Journal of Biomedical Materials Research* 38 (1), 11–16.
- Lewis, G., 2003. Fatigue testing and performance of acrylic bone-cement materials: State-of-the-art review. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 66 (1), 457–486.
- Li, T., Weng, X., Bian, Y., *et al.*, 2015. Influence of nano-HA coated bone collagen to acrylic (polymethylmethacrylate) bone cement on mechanical properties and bioactivity. *PloS One* 10 (6), e0129018.
- Liebedörfer, A., Schmitz, B., Wenz, R., Specht, R., Bonath, K., 1995. Experimental studies on a new bone cement: Hydroxyapatite composite resin. In: *Proceedings of the 21st Annual Meeting of the Society for Biomaterials*. San Francisco, USA.
- Lin, L.C., Chang, S.J., Kuo, S.M., Chen, S.F., Kuo, C.H., 2005. Evaluation of chitosan/ β -tricalcium phosphate microspheres as a constituent to PMMA cement. *Journal of Materials Science: Materials in Medicine* 16 (6), 567–574.
- Liu-Snyder, P., Webster, T.J., 2008. Developing a new generation of bone cements with nanotechnology. *Current Nanoscience* 4 (1), 111–118.
- Magnan, B., Bondi, M., Maluta, T., *et al.*, 2013. Acrylic bone cement: Current concept review. *Musculoskeletal Surgery* 97 (2), 93–100.
- Markatos, K., Brilakis, E., Elstathopoulos, N., 2010. The evolution in reconstructive orthopaedic surgery- arthroplasty and its implants after World War II. *Acta Orthopaedica et Traumatologica Hellenica* 61 (4), 203–207.
- Marrs, B.H., 2007. Carbon Nanotube Augmentation of a bone cement polymer. University of Kentucky Doctoral Dissertations, 514.
- Mostafa, N.Y., Brown, P.W., 2007. Computer simulation of stoichiometric hydroxyapatite: Structure and substitutions. *Journal of Physics and Chemistry of Solids* 68 (3), 431–437.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., *et al.*, 2004. Electric field effect in atomically thin carbon films. *Science* 306 (5696), 666–669.
- Ogiso, M., 1992. Bone calcification on the hydroxyapatite dental implant. bone-hydroxyapatite interface. *Journal of Long-Term Effects of Medical Implants* 2, 137–148.
- Ormsby, R., McNally, T., Mitchell, C., Dunne, N., 2010. Incorporation of multiwalled carbon nanotubes to acrylic based bone cements: Effects on mechanical and thermal properties. *Journal of the Mechanical Behavior of Biomedical Materials* 3 (2), 136–145.
- Ormsby, R., McNally, T., O'Hare, P., *et al.*, 2012. Fatigue and biocompatibility properties of a poly (methyl methacrylate) bone cement with multi-walled carbon nanotubes. *Acta Biomaterialia* 8 (3), 1201–1212.
- Pahlevanzadeh, F., Bakhsheshi-Rad, H.R., Hamzah, E., 2018. In-vitro biocompatibility, bioactivity, and mechanical strength of PMMA-PCL polymer containing fluorapatite and graphene oxide bone cements. *Journal of the Mechanical Behavior of Biomedical Materials* 82, 257–267.
- Pahlevanzadeh, F., Bakhsheshi-Rad, H., Ismail, A.F., Aziz, M., Chen, X., 2019a. Development of PMMA-Mon-CNT bone cement with superior mechanical properties and favorable biological properties for use in bone-defect treatment. *Materials Letters* 240, 9–12.
- Pahlevanzadeh, F., Bakhsheshi-Rad, H.R., Ismail, A.F., Aziz, M., 2019b. Apatite-forming ability, cytocompatibility, and mechanical properties enhancement of poly methyl methacrylate-based bone cements by incorporating of baghdadite nanoparticles. *International Journal of Applied Ceramic Technology* 16 (5), 2006–2019.
- Parvizifard, M., Karbasi, S., Salehi, H., Soleymani Eil Bakhtiari, S., 2020. Evaluation of physical, mechanical and biological properties of bioglass/titania scaffold coated with poly (3-hydroxybutyrate)-chitosan for bone tissue engineering applications. *Materials Technology* 35 (2), 75–91.
- Paz, E., Forriol, F., Del Real, J.C., Dunne, N., 2017. Graphene oxide versus graphene for optimisation of PMMA bone cement for orthopaedic applications. *Materials Science and Engineering: C* 77, 1003–1011.
- Perek, J., Pilliar, R.M., 1992. Fracture toughness of composite acrylic bone cements. *Journal of Materials Science: Materials in Medicine* 3 (5), 333–344.
- Phakatkarn, A.H., Shirdar, M.R., Qi, M.L., *et al.*, 2020. Novel PMMA bone cement nanocomposites containing magnesium phosphate nanosheets and hydroxyapatite nanofibers. *Materials Science and Engineering: C* 109, 110497.
- Pino-Mínguez, J., Jorge-Mora, A., Couceiro-Otero, R., García-Santiago, C., 2015. Study of the viability and adhesion of osteoblast cells to bone cements mixed with hydroxyapatite at different concentrations to use in vertebral augmentation techniques. *Revista Española de Cirugía Ortopédica y Traumatología (English Edition)* 59 (2), 122–128.
- Quan, C., Tang, Y., Liu, Z., *et al.*, 2016. Effect of modification degree of nanohydroxyapatite on biocompatibility and mechanical property of injectable poly (methyl methacrylate)-based bone cement. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 104 (3), 576–584.
- Rhee, S.H., Hwang, M.H., Si, H.J., Choi, J.Y., 2003. Biological activities of osteoblasts on poly(methyl methacrylate)/silica hybrid containing calcium salt. *Biomaterials* 24, 901–906.
- Russo, T., Gloria, A., De Santis, R., *et al.*, 2017. Preliminary focus on the mechanical and antibacterial activity of a PMMA-based bone cement loaded with gold nanoparticles. *Bioactive Materials* 2 (3), 156–161.
- Rajakumar, G., Zhang, X.H., Gomathi, T., *et al.*, 2020. Current Use of Carbon-Based Materials for Biomedical Applications—A Prospective and Review. *Processes* 8 (3), 355.

- Ricker, A., Liu-Snyder, P., Webster, T.J., 2008. The influence of nano MgO and BaSO₄ particle size additives on properties of PMMA bone cement. *International Journal of Nanomedicine* 3 (1), 125.
- Sa, Y., Yu, N., Wolke, J.G., *et al.*, 2017. Bone response to porous poly (methyl methacrylate) cement loaded with hydroxyapatite particles in a rabbit mandibular model. *Tissue Engineering Part C: Methods* 23 (5), 262–273.
- Saha, S., Pal, S., 1984. Mechanical properties of bone cement: A review. *Journal of Biomedical Materials Research* 18 (4), 435–462.
- Samad, H.A., Jaafar, M., Othman, R., Kawashita, M., Razak, N.H., 2011. New bioactive glass-ceramic: Synthesis and application in PMMA bone cement composites. *Bio-Medical Materials and Engineering* 21 (4), 247–258.
- Shinzato, S., Nakamura, T., Kawanabe, K., Kokubo, T., 2004. *In vivo* aging test for a bioactive bone cement consisting of glass bead filler and PMMA matrix. *Journal of Biomedical Materials Research. Part B Applied Biomaterials* 68, 132–139.
- Singh, M.K., Shokuhfar, T., Gracio, J.J., *et al.*, 2008. Hydroxyapatite modified with carbon-nanotube-reinforced poly (methyl methacrylate): A nanocomposite material for biomedical applications. *Advanced Functional Materials* 18 (5), 694–700.
- Singh, B.G., Baburao, C., Pispatis, V., *et al.*, 2012. Carbon nanotubes. A novel drug delivery system. *International Journal of Research in Pharmacy and Chemistry* 2 (2), 523–532.
- Slane, J., Vivanco, J., Meyer, J., Ploeg, H.L., Squire, M., 2014. Modification of acrylic bone cement with mesoporous silica nanoparticles: Effects on mechanical, fatigue and absorption properties. *Journal of the Mechanical Behavior of Biomedical Materials* 29, 451–461.
- Soleymani, Eil Bakhtiari, S., Karbasi, S., Tabrizi, S.A., Ebrahimi-Kahrizsangi, R., 2019. Chitosan/MWCNTs composite as bone substitute: Physical, mechanical, bioactivity, and biodegradation evaluation. *Polymer Composites* 40 (S2), E1622–E1632.
- Soleymani Eil Bakhtiari, S., Bakhsheshi-Rad, H.R., Karbasi, S., *et al.*, 2020a. Polymethyl methacrylate-based bone cements containing carbon nanotubes and graphene oxide: an overview of physical, mechanical, and biological properties. *Polymers* 12 (7), 1469.
- Soleymani Eil Bakhtiari, S., Bakhsheshi-Rad, H.R., Karbasi, S., *et al.*, 2020b. Poly (methyl methacrylate) bone cement, its rise, growth, downfall and future. *Polymer International*. doi:10.1002/pi.6136.
- Soleymani Eil Bakhtiari, S., Karbasi, S., Hassanzadeh Tabrizi, S.A., Ebrahimi-Kahrizsangi, R., Salehi, H., 2020c. Evaluation of the effects of chitosan/multiwalled carbon nanotubes composite on physical, mechanical and biological properties of polymethyl methacrylate-based bone cements. *Materials Technology* 35 (5), 267–280.
- Standard, ASTM STD E399, ASTM STD E399, 1989. Standard test method for plane-strain fracture toughness of metallic materials. *Annual book of ASTM standards*, Part 3.01. Philadelphia: American Society for Testing and Materials, pp. 487–511.
- Standard, I.S., 2002. International Standard ISO 5833, 2002, Implants for Surgery – Acrylic Resin Cements. International Standards Organization.
- Standard, A.S., 2006. F451-99a. Standard Specification for Acrylic Bone Cement. West Conshohocken, PA: ASTM International.
- Sun, X., Wu, Z., He, D., *et al.*, 2019. Bioactive injectable polymethylmethacrylate/silicate bioceramic hybrid cements for percutaneous vertebroplasty and kyphoplasty. *Journal of the Mechanical Behavior of Biomedical Materials* 96, 125–135.
- Sundfeldt, M., Carlsson, L.V., Johansson, C.B., Thomsen, P., Gretzer, C., 2006. Aseptic loosening, not only a question of wear: A review of different theories. *Acta Orthopaedica* 77, 177–197.
- Tan, H., Guo, S., Yang, S., Xu, X., Tang, T., 2012. Physical characterization and osteogenic activity of the quaternized chitosan-loaded PMMA bone cement. *Acta Biomaterialia* 8 (6), 2166–2174.
- Tang, Y., Chen, L., Wu, Z., Zhao, K., Tan, Q., 2017. Fabrication of injectable and expandable PMMA/PAASf bone cements. *Composites Science and Technology* 146, 203–209.
- Tavakoli, M., Bakhtiari, S.S., Karbasi, S., 2020a. Incorporation of chitosan/graphene oxide nanocomposite in to the PMMA bone cement: Physical, mechanical and biological evaluation. *International Journal of Biological Macromolecules* 149, 783–793.
- Tavakoli, M., Karbasi, S., Bakhtiari, S.S.E., 2020b. Evaluation of physical, mechanical, and biodegradation of chitosan/graphene oxide composite as bone substitutes. *Polymer-Plastics Technology and Materials* 59 (4), 430–440.
- Tsukeoka, T., Suzuki, M., Ohtsuki, C., *et al.*, 2006. Mechanical and histological evaluation of a PMMA-based bone cement modified with γ -methacryloxypropyltrimethoxysilane and calcium acetate. *Biomaterials* 27 (21), 3897–3903.
- Tunney, M.M., Brady, A.J., Buchanan, F., Newe, C., Dunne, N.J., 2008. Incorporation of chitosan in acrylic bone cement: Effect on antibiotic release, bacterial biofilm formation and mechanical properties. *Journal of Materials Science: Materials in Medicine* 19 (4), 1609–1615.
- Usui, Y., Haniu, H., Tsuruoka, S., Saito, N., 2012. Carbon nanotubes innovate on medical technology. *Medicinal Chemistry* 2 (1), 1–6.
- Valencia Zapata, M.E., Mina Hernandez, J.H., Grande Tovar, C.D., *et al.*, 2019. Novel bioactive and antibacterial acrylic bone cement nanocomposites modified with graphene oxide and chitosan. *International Journal of Molecular Sciences* 20 (12), 2938.
- Valencia Zapata, M.E., Mina Hernandez, J.H., Grande Tovar, C.D., 2020. Acrylic Bone Cement Incorporated with Low Chitosan Loadings *Polymers* 12 (7), 1617.
- Venkatesan, J., Kim, S.K., 2010. Chitosan composites for bone tissue engineering – An overview. *Marine Drugs* 8 (8), 2252–2266.
- Webb, J.C., Spencer, R.F., 2007. The role of polymethylmethacrylate bone cement in modern orthopaedic surgery. *The Journal of Bone and Joint Surgery* 89 (7), 851–857. British volume.
- Wekwejt, M., Michalska-Sionkowska, M., Bartmański, M., *et al.*, 2020. Influence of several biodegradable components added to pure and nanosilver-doped PMMA bone cements on its biological and mechanical properties. *Materials Science and Engineering: C* 117, 111286.
- Wang, C., Yu, B., Fan, Y., *et al.*, 2019. Incorporation of multi-walled carbon nanotubes to PMMA bone cement improves cytocompatibility and osseointegration. *Materials Science and Engineering: C* 103, 109823.
- Wu, J., Xu, S., Qiu, Z., *et al.*, 2016. Comparison of human mesenchymal stem cells proliferation and differentiation on poly (methyl methacrylate) bone cements with and without mineralized collagen incorporation. *Journal of Biomaterials Applications* 30 (6), 722–731.
- Wolf-Brandstetter, C., Roessler, S., Storch, S., *et al.*, 2013. Physicochemical and cell biological characterization of PMMA bone cements modified with additives to increase bioactivity. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 101 (4), 599–609.
- Xue, L., Lu, X., Wei, H., *et al.*, 2014. Bio-inspired self-cleaning PAAS hydrogel released coating for marine antifouling. *Journal of Colloid and Interface Science* 421, 178–183.
- Xu, Y., Wang, Y., Cui, L., 2013. An efficient functionalization method for the multiwalled carbon nanotubes and their applications in PMMA bone cement. *Sensors & Transducers* 21 (5), 36–41.
- Yang, J.M., Lu, C.S., Hsu, Y.G., Shih, C.H., 1997. Mechanical properties of acrylic bone cement containing PMMA-SiO₂ hybrid sol-gel material. *Journal of Biomedical Materials Research* 38 (2), 143–154.
- Yuan, Q., Shah, J., Hein, S.R., Misra, R.D., 2010. Controlled and extended drug release behavior of chitosan-based nanoparticle carrier. *Acta Biomaterialia* 6 (3), 1140–1148.
- Zhang, Y., Bai, Y., Yan, B., 2010. Functionalized carbon nanotubes for potential medicinal applications. *Drug Discovery Today* 15 (11–12), 428–435.
- Zapata, M.E., Hernandez, J.H., Grande Tovar, C.D., *et al.*, 2020. Osseointegration of Antimicrobial Acrylic Bone Cements Modified with Graphene Oxide and Chitosan *Applied Sciences* 10 (18), 6528.
- Zebarjad, S.M., Sajjadi, S.A., Ebrahimi Sdrabadi, T., Yaghmaei, A., Naderi, B., 2011. A study on mechanical properties of PMMA/hydroxyapatite nanocomposite. *Engineering* 3 (08), 795–801.

Hydrogel Composite Films for Wound Healing

Ikram U Khan and Huma Mahmood, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Yasser Shahzad, Department of Pharmacy, COMSATS University Islamabad, Lahore, Pakistan

Sajid Asghar and Haroon K Syed, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

© 2021 Elsevier Inc. All rights reserved.

Drug Delivery

Drug delivery can be described as “the methods to administer the pharmaceutical ingredients so as to achieve therapeutic effects in humans or animals” (Bhowmik *et al.*, 2012; Tiwari *et al.*, 2012). Oral and parenteral routes are frequently employed for drug administration but have several limitations such as oral route is associated with high drug susceptibility to enzymes in gastrointestinal tract (Liu *et al.*, 2003), first pass effect, poor absorption of peptides and proteins, and poor patient compliance for those who are unable to take any oral medication (Rathbone *et al.*, 1994). Similarly, parenteral route has several limitations as being painful, lack of self administration, local injury, thrombus formation, and hypersensitivity reactions (Bruce and Wong, 2001). In literature, it is suggested that skin, one of the largest organs of body may be used as an alternative route for several drugs either by transdermal drug delivery or topically for localize pharmacological response (Tiwari *et al.*, 2012). Both systems are suitable for patients who are unable to take any oral medication, thus enhances patient compliance (Mazzitelli *et al.*, 2013) and provides control drug release for prolong period (Grampurohit *et al.*, 2011).

Drug Delivery Through Skin

Being one of the largest organs of body, skin occupies an area of about two meter square (Hopewell, 1990). Skin has three layered (epidermis, dermis and hypodermis) complex structure (Metcalf and Ferguson, 2007), which acts as a main barrier and separates the underlying tissues from outer environment (Kamoun *et al.*, 2017), regulates temperature, prevents the electrolytes and water loss, and impedes entry of toxic chemicals, allergens, microbes and irritants. Skin can be used for both transdermal delivery (systemic effect) and topical delivery (local effect) of several drugs (Prausnitz and Langer, 2008).

Wound

Wound may be defined as any disruption, break or disorder in normal skin structure and functions (Boateng *et al.*, 2008). A wound primarily may result from any physical, thermal or chemical skin damage while secondary cause include several diseases (carcinoma, diabetes or ulcers) and any surgical intervention. Depending upon the type of skin tissues and cells that undergo disruption, wounds may range from superficial to full thickened wound as shown in Fig. 1.

When outermost layer is affected by temperature, extreme pressure, any chemical or cut, it is a superficial wound; when epidermis and dermis layer along with hair follicles and blood vessels are affected then it is partially thickened wound; while any injury to hypodermal fats or deeper tissues results in full thickened wounds (Sarheed *et al.*, 2016; Boateng *et al.*, 2008). Wounds can also be classified as acute and chronic wounds depending upon their healing time. Acute wounds requires limited time to heal, and no serious complications are involved. Chronic wounds require prolonged healing time and are characterized by prolonged inflammation, presence of microbial pathogens, persistent infection and impaired healing (Boateng *et al.*, 2008).

Wound healing

A biological process that follows the general phenomenon of tissue regeneration and growth is referred as wound healing (Reinke and Sorg, 2012). Healing process is comprised of following stages; hemostasis, inflammation, proliferation, and remodeling as depicted in Fig. 2 (Sarheed *et al.*, 2016).

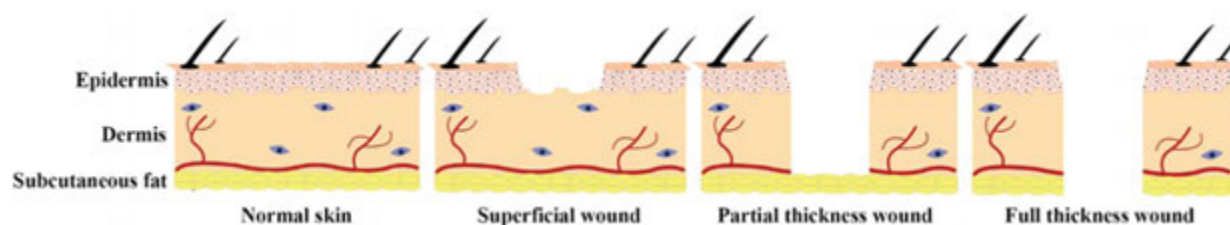


Fig. 1 Classification of wounds. Adapted from Da, L.-C., Huang, Y.-Z., Xie, H.-Q., 2017. Progress in development of bioderived materials for dermal wound healing. *Regenerative Biomaterials* 4, 325–334.

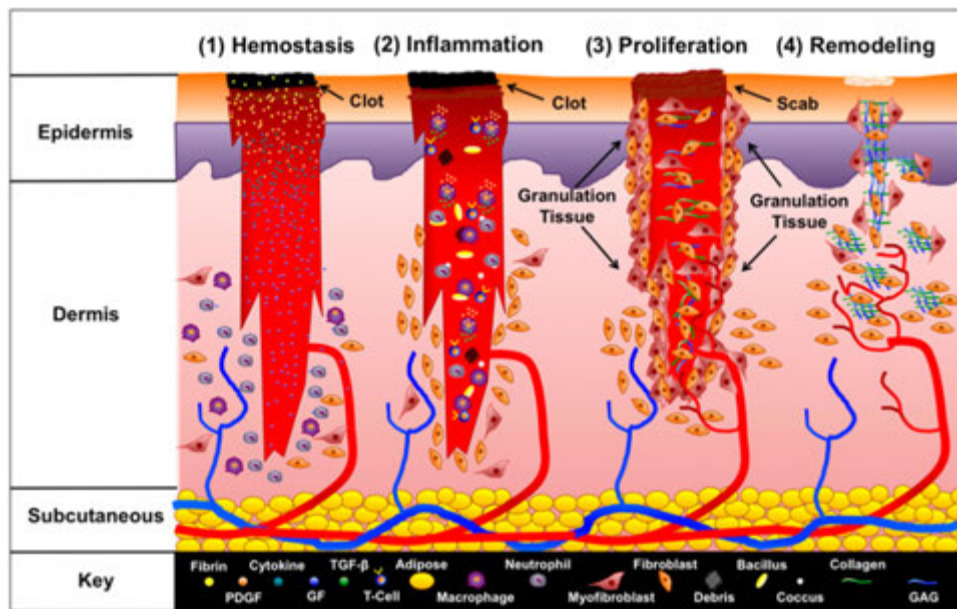


Fig. 2 Various stages of wound healing process. Reproduced from Mellott, A.J., Zamierowski, D.S., Andrews, B.T., 2016. Negative pressure wound therapy in maxillofacial applications. *Dentistry Journal* 4, 30.

(1) *Hemostasis*

Hemostasis is characterized by bleeding, immediately after an injury or trauma and involves flushing of antigens and bacteria from wound site. Released cytokines and inflammatory mediators causing platelet aggregation (Boateng *et al.*, 2008).

(2) *Inflammation*

This stage starts simultaneously with hemostatic stage and lasts for about 72 h. It is characterized by release of prostaglandins and histamine from mast cells, monocytes migrate to wound area causing edema and inflammation (Sarheed *et al.*, 2016).

(3) *Proliferative phase*

Proliferative phase is characterized by production of growth factors, which initiate the process of angiogenesis and epithelial thickening with collagen deposition (Boateng *et al.*, 2008).

(4) *Remodeling*

Remodeling is characterized by re-epithelialization, connective tissue formation, wound contraction, and wound closure.

Wound dressings

Wound dressings not only covers the wound but also helps in regeneration of epidermal tissues during healing process (Adamian *et al.*, 2004). These dressings act as physical barrier and protect the wounds from invading microorganisms (Mogoşanu and Grumezescu, 2014). Effective wound dressing maintains the moisture at wound area which helps to transport the keratinocytes, growth factors and enzymes (Moura *et al.*, 2013) to promote healing (Dumville *et al.*, 2013).

In ancient periods, wound dressings were prepared from crude plants, animal fats and honey which have antimicrobial properties (Inngjerdingen *et al.*, 2004). However, direct application of crude plant was harmful, as it would contain chemicals or microorganisms, which may cause infection. So, this recognition led to development of dressings having effective antimicrobial moiety and enzymatic agents (Thomas, 2000). Until 1962, it was thought that wound healing would be faster if kept dried. This concept was changed by work of "Winter", who, for the first time, designed the moist wound films and revealed that healing is faster in wet environment as it helps in epithelialization and faster cell proliferation (Kamoun *et al.*, 2017).

Requirements for wound dressings

Ideal dressings must have ability to keep moist environment at wound surface, remove exudates, provide protection from microbes and promote healing (Kamoun *et al.*, 2017). Ideal dressings must provide mechanical protection, thermal insulation and oxygen exchange and are compatible with biological systems (Altioek *et al.*, 2010). Furthermore, it must be non-allergenic, biodegradable, non-toxic and cost effective (Kokabi *et al.*, 2007).

Classification of wound dressings

Wound dressings can be classified in several ways; depending on their functions (Queen *et al.*, 2004), on the basis of material used for their production (Purna and Babu, 2000), and on their physical form as shown in Fig. 3. Most commonly, dressings are classified as traditional and modern dressings (Thomas, 2000).

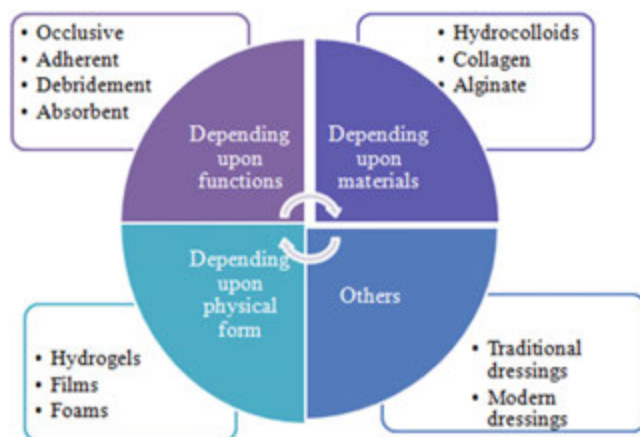


Fig. 3 Classification of wound dressings.

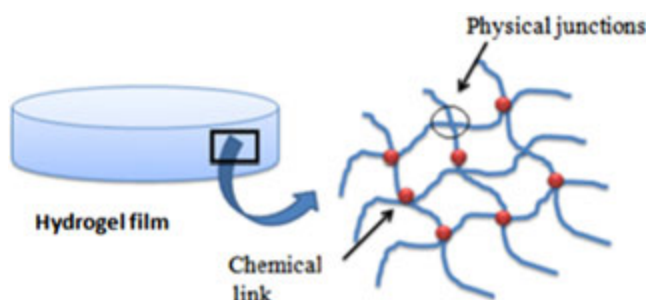


Fig. 4 Structure of thin hydrogel films.

Traditional dressings

Traditional dressings include bandages, cotton wools, and gauzes. These dressings, being easy to fabricate, easy to use and low cost, were frequently used till 1990s (Edwards *et al.*, 2001). These dressings are dry in nature and do not maintain moisture at wound site, thus, leading to dehydration which promotes microbial growth at wound site (Van Rijswijk, 2006).

Modern dressings

These dressings are most preferred ones as they keep the wound site moist, which helps in wound repairing and healing. Modern dressings are further classified as biological dressings (comprised of biomaterials) and artificial dressings (composed of non-biological or synthetic materials/polymers) (Kamoun *et al.*, 2017).

Hydrogel Films

Generally the term “gel” refers to a viscoelastic deformable network in continuous medium that is either gas or liquid (Mateescu *et al.*, 2012). When continuous phase is gas then system is known as aerogel, and in case of liquid, system is generally termed as lyogel, and for water it is referred as hydrogel (Künzler, 2002). Hydrogel films are defined as “three dimensional crosslinked thin films of hydrophilic polymers which have tendency to absorb large amount of water without solubilizing or losing integrity due to strong junctions between its segments” (Ahmed, 2015) or can be defined as “soft, flexible, water swollen, three dimensional crosslinked macromolecular network of hydrophilic polymers” (Ye and Loh, 2013). Functional groups of hydrophilic polymers provide the capability to absorb water, while crosslinks between the polymeric chains prevents their disintegration in desired media.

In hydrogel films, polymers are crosslinked via physical or chemical interactions (Fig. 4); physical interactions are mechanically weak, reversible and may be effected by environmental factors like temperature, ionic strength and pH. On the other hand, chemical interactions are more stable and strong, but chemical agents may be toxic (Uliniuc *et al.*, 2013).

Properties and applications of hydrogel films

- (1) Hydrogel films have gained considerable attention due to their unique properties like ability to retain high water content, high aqueous stability, biocompatibility with biological system, softness, elasticity and can load variety of agents in high enough concentration and release them in controlled manner (Mali *et al.*, 2017).

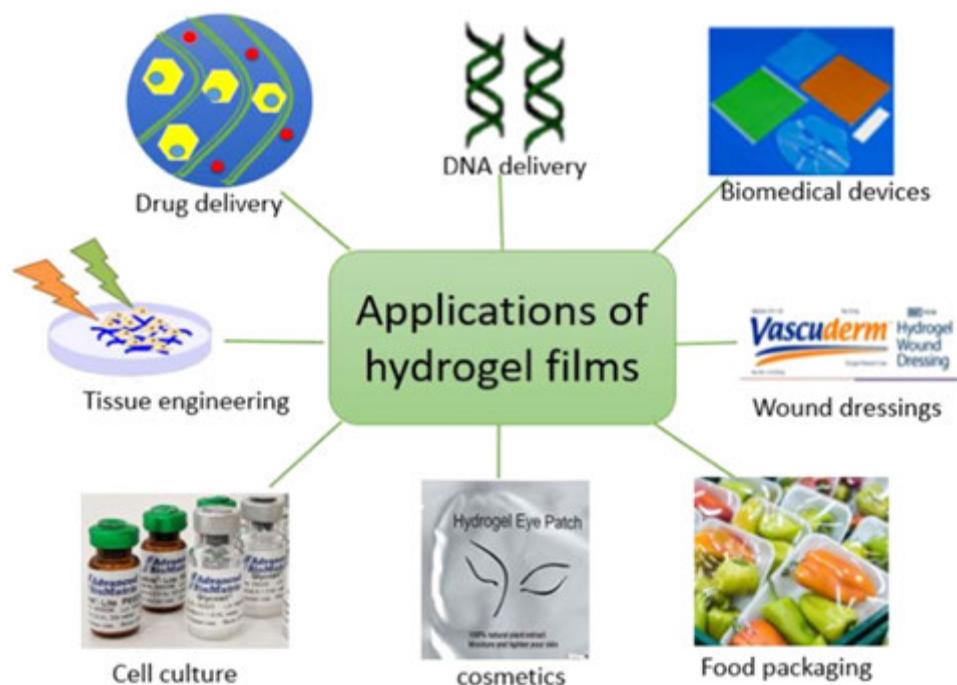


Fig. 5 Applications of hydrogel films.

- (2) Hydrogels have ability to mimic the physical, chemical, electrical, and biological properties of biological tissues (Gaharwar *et al.*, 2014).
- (3) Hydrogel films have remarkable mechanical, optical, and surface properties which make it a promising material for diverse applications (Seliktar, 2012).
- (4) Hydrogels have ability to hold up to 40 folds of more water as compared to their initial dry weight (Gaharwar *et al.*, 2014).
- (5) One of the remarkable properties of hydrogel films is their porous nature, which allows high drug loading and high local concentration at targeted site (Zhao *et al.*, 2015).
- (6) Hydrogel films have been proposed for several biotechnological and biomedical applications like wound healing (Thu *et al.*, 2012), tissue engineering, cell adhesion (Hoare and Kohane, 2008), cosmetics, and food industry (Fig. 5; Ejaz *et al.*, 2018).
- (7) Biodegradability of hydrogels is an essential factor for biomedical applications.
- (8) Hydrogel films have also tailored the vast applications in immune-modulation, stem cell engineering, cellular and molecular therapies, in vitro diagnostics and anti-cancer research (Fig. 5; Gaharwar *et al.*, 2014).

Composite Hydrogel Films

Mostly, one polymer is exploited for preparation of hydrogels network but it lacks biological and mechanical properties essential for biomedical application. As single polymeric network, structure is too flexible that leads to premature drug release at targeted site. To overcome these problems, multiple entities are incorporated into hydrogel system to formulate a composite material (Gaharwar *et al.*, 2014).

Composite hydrogel films can be defined as “the systems which contain two or more than two constituent materials with different physicochemical properties, where individual constituent materials remain distinct and separate but impart different and better characteristics to the final composite system” (Ye and Loh, 2013). Main purpose of fabrication of composite films is strength enhancement and reinforcement. Recently, composite hydrogel films have gained much attention in drug delivery, biomedical applications, medical devices, cosmetics as well as in food industry due to their reliability and high stability (Roy and Rhim, 2020; Alavi *et al.*, 2019; Ejaz *et al.*, 2018; Liu *et al.*, 2008).

Synthesis of Hydrogel Films

Main principle for synthesis of hydrogel films is crosslinking of polymeric chains, after which films show viscoelastic or pure elastic behavior. Crosslinking is achieved by either addition of crosslinking agents, through chemical modification or by exposure of high energy radiations. These methods of crosslinking are categorized in two main categories i.e., physical crosslinking and chemical crosslinking. Chemically crosslinked films are more stable as compared to physically crosslinked films but chemical crosslinking agents are toxic. Therefore, both methods have their own benefits as well as drawbacks discussed under respective details. Different methods involved in preparation of films are shown in Fig. 6.

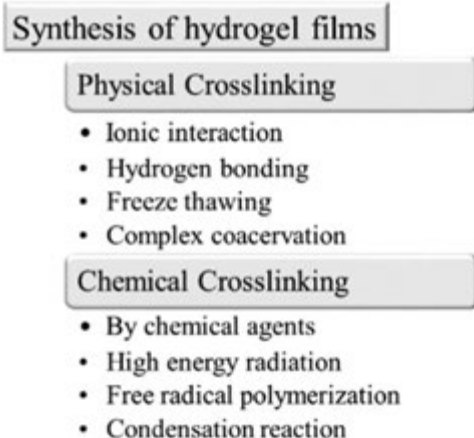


Fig. 6 Various method employed to develop hydrogel films.

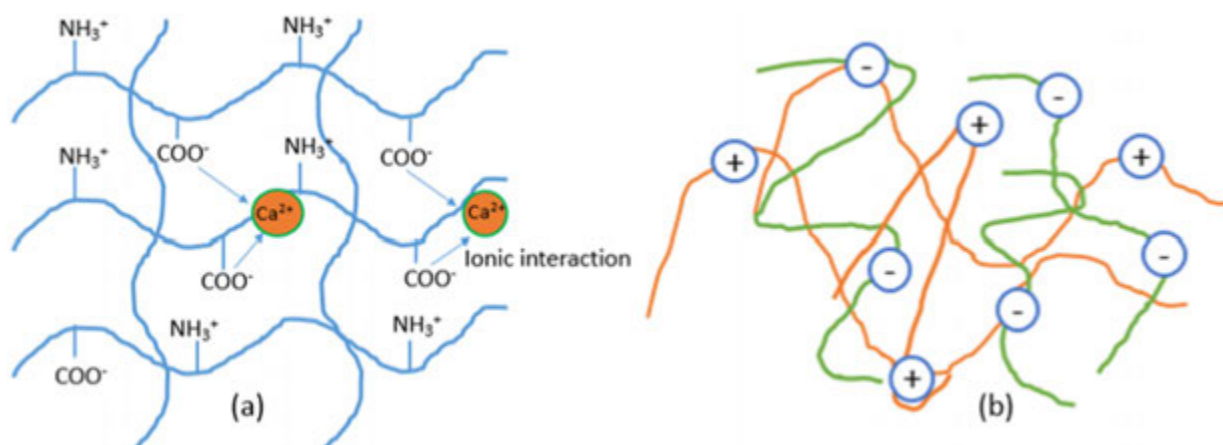


Fig. 7 Physical crosslinking in polymers (a) ionic interaction (b) complex coacervation.

Physical crosslinking

Ionic interactions

Ionic crosslinking is carried out by addition of di or tri valent counter ions in polymeric solution under specific conditions i.e., room temperature and at physiological pH. For example, polysaccharides are crosslinked via calcium ions (counter ion) (Pereira *et al.*, 2013b) as shown in Fig. 7(a). This method provides mechanically stable gels with uniform structure which are easily degraded in physiological solution (Ali and Ahmed, 2018). Interestingly, these gels can be easily destabilized by extracting the counter ions through chelating agents (Ullah *et al.*, 2015). However, in this method it is difficult to control the gelation rate as it increases with increasing the concentration of polymer and temperature.

Hydrogen bonding

This method is utilized for polymers that have carboxyl groups, which undergo protonation leading to hydrogen bonding and show pH dependent swelling (Akhtar *et al.*, 2016). For this purpose, polymeric solution is dispersed into acidic solution (0.1 M HCl) where sodium ions are replaced by hydrogen ions leading to hydrogen bonding and formation of elastic hydrogel (Takigami *et al.*, 2007).

Freeze thaw method

Freeze thaw method is one of the promising methods for hydrogel films synthesis especially for polysaccharide based polymers, where strong, highly porous, interconnected, rubbery and elastic gels are produced (Varaprasad *et al.*, 2017). In this method polymer solution is frozen at low temperature (-20°C to -80°C) followed by melting at room temperature (Ali and Ahmed, 2018). Gel formation is attributed to formation of microcrystals of polymers that act as crosslinking sites in network. Properties of finally formed gel depends upon the molecular weight of polymer, concentration of polymer in water, temperature, number and duration of freezing cycles, pH and rate of thawing. Mechanical properties of films can be enhanced by increasing the freeze thaw cycles and by lowering the temperature (Ullah *et al.*, 2015). Ahmed *et al.*, used this method for preparation of PVA-PEG based films for wound healing (Ahmed *et al.*, 2018).

Complex coacervation

Principle of complex coacervation is the usage of oppositely charged polymers i.e., polycationic and polyanionic polymers which when aggregate together, form a complex as shown in [Fig. 7\(b\)](#), depending upon pH and polymer concentration ([Ali and Ahmed, 2018](#)).

Chemical crosslinking

Although, physical crosslinking method has the advantage of preparing gel matrix without addition of any crosslinking agent but these physical junctions do not have enough mechanical strength while chemically crosslinked films are mechanically strong. Chemical crosslinking involves following methods.

Addition reaction/by chemical agents

This method involves the addition of chemicals such as glutaraldehyde, PEG, glyoxal, epichlorohydrin, and polyaldehydes etc. which form covalent linkages between polymers. These covalent bonds are formed by reaction of functional groups of polymers (OH, COOH, and NH₂) with complementary reactivity such as an amine-carboxylic acid or an isocyanate-OH/NH₂ reaction ([Varaprasad et al., 2017](#)).

High energy radiation method

This method is also named as “radiation grafting” where high-energy radiations such as gamma radiations or electron beam are used to initiate the free radical polymerization reaction. Mostly unsaturated compounds are polymerized by this method where hydrophilic polymers on exposure to gamma radiations/electron beam are derivatized through polymerizable groups and form radicals on polymeric chains via homolytic scission ([Zhao et al., 2003](#); [Zhai et al., 2002](#)). These radiations assist the water molecules to form the hydroxyl group, which attack polymer chains and form micro-radicals. Aggregation of different micro-radicals of different polymer chains lead to formation of covalent bonds resulting in crosslinked structure. Although, this method does not use any toxic chemical agents as well as whole process is carried out at room temperature and physiological pH. However, this method yields non-biodegradable gels ([Varaprasad et al., 2017](#)).

Free radical polymerization technique

Hydrogel films are efficiently crosslinked by this method where low molecular weight monomers are crosslinked in presence of crosslinking agent through polymerization technique. Free radical initiators such as potassium or ammonium persulfate or benzoyl peroxide are used to initiate the process of polymerization, which results in rapid gel formation under mild temperature conditions.

Condensation reaction

Polyamides and polyesters are synthesized by condensation reaction method, where reaction takes place among NH₂ or OH groups with COOH respectively. For crosslinking of hydrophilic polymers through condensation reaction, the most efficient reagent is N,N-(3-dimethylaminopropyl)-N-ethyl carbodiimide (EDC) having amide group ([Akhtar et al., 2016](#)). PVA and gelatin hydrogels have been synthesized by using EDC ([Ray et al., 2010](#); [Kuijpers et al., 2000](#)).

Why Hydrogel Films as Wound Dressings?

Hydrogel films can act as favorable dressings for wound healing due to their intrinsic properties of absorbing and retaining exudates at wound site, which promotes the fibroblast formation, cell proliferation and keratinocytes migration. Highly porous nature of hydrogel films allows the transportation of bioactive compounds such as antibiotics and other pharmaceutical ingredients at wound site. These bioactive compounds are entrapped in film matrix during gelling process and are exchanged with exudate, when film meets wound surface. Tight mesh size of film protects the wound from microbial infection and high water content of hydrogel films provides the required elasticity, flexibility and tissue like structure ([Kamoun et al., 2017](#)).

Composite Hydrogel Films as Wound Dressing*Composite films containing natural polymers*

Interest towards the use of natural polymers has increased specially in biomedical and regenerative field due to their tissue repairing and skin regeneration properties ([Huang and Fu, 2010](#)). Furthermore, natural polymers provide the advantage of being biodegradable and biocompatible with biological system. Vast variety of natural polymers are utilized for fabrication of composite hydrogel films for wound healing. In forthcoming sections, we will discuss most important polymers with relevant examples and studies carried out by various eminent research groups.

(a) Polysaccharides

Polysaccharides have excellent properties, which make this group one of the widely used polymeric group in biomedical field. These include high water solubility, swellability, non-toxicity, biodegradability, susceptibility to enzymatic digestion in body as well as high tissue compatibility and some of them are helpful to enhance healing process. Thus make it potential candidate for biomedical applications such as skin regeneration, tissue engineering and wound management ([Varaprasad et al., 2017](#)).

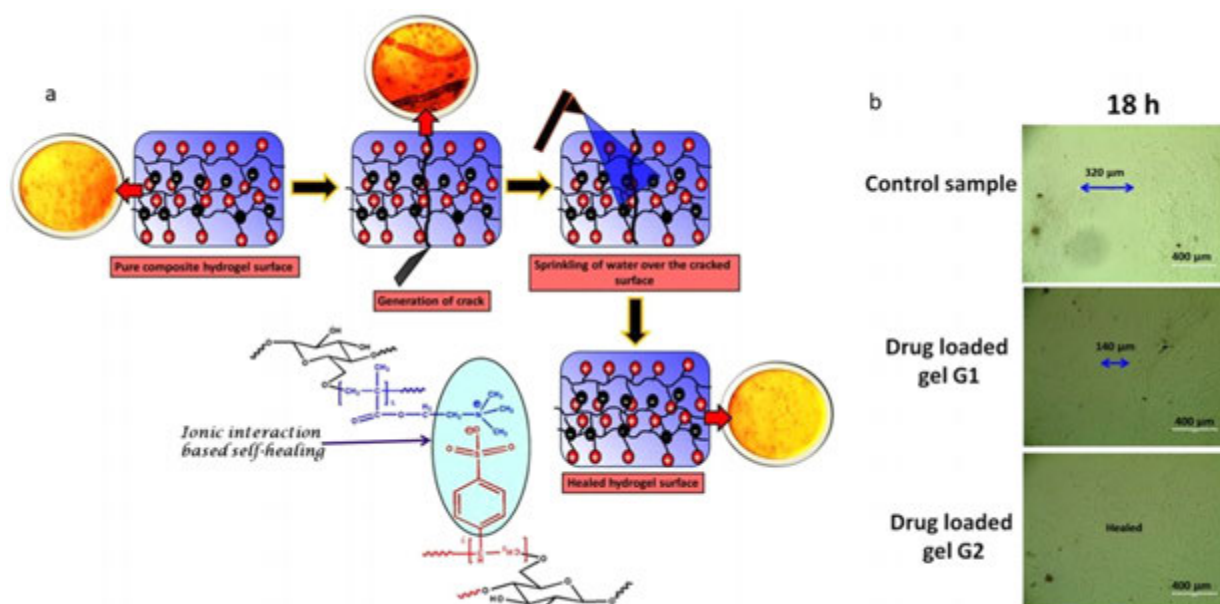


Fig. 8 (a) Self-healing capability of curcumin entrapped gelatin/iBC hydrogel films was assessed by “scratch and heal” test which shows the iBC contributes in healing of damaged film by developing ionically interlocked structure in the presence of a buffer solution. (b) Wound healing assay of on NIH-3 T3 fibroblast cells after treatment with pure ionically modified gelatin hydrogel film (control) and drug-loaded (G1 and G2 contains 7% and 12% curcumin respectively) ionically modified gelatin hydrogel film. Reproduced from Khamrai, M., Banerjee, S.L., Paul, S., Samanta, S., Kundu, P.P., 2019. Curcumin entrapped gelatin/ionically modified bacterial cellulose based self-healable hydrogel film: An eco-friendly sustainable synthesis method of wound healing patch. *International Journal of Biological Macromolecules* 122, 940–953, with permission from Elsevier.

i. Cellulose

Cellulose is a hydrophilic polysaccharide biomaterial with excellent properties such as biocompatibility, oxygen and nutrients permeability, high porosity etc. Cellulose itself have no antibacterial property (Kabir *et al.*, 2018) so, its hydrogel film dressing must contain other bactericidal agents. Cellulose based dressings are widely used but cause maceration of wound and pain during removal. These drawbacks can be overcome by combing it with other polymers or using hydrogels (Pinho and Soares, 2018). To overcome the said drawbacks, cellulose and its derivatives based composite hydrogel films have been fabricated in combination with other natural polymers. For e.g., bacterial cellulose from *Gluconacetobacter xylinus* was grafted with cationic and anionic segments to get ionically modified self-assembled bacterial cellulose (iBC) and later blended with gelatin to develop hydrogel films having inherent self-healing capability as shown in Fig. 8. Here, gelatin is caged in iBC and thus provides mechanical strength to films. Furthermore, these films were loaded with curcumin, which showed superior antibacterial and wound healing properties as compared to blank films. This difference is due to the presence of curcumin, which have antioxidant and antibacterial properties, and promotes cell proliferation and migration (Khamrai *et al.*, 2019).

In another study, sodium carboxymethyl cellulose/hydroxypropyl methylcellulose was crosslinked with citric acid and incorporated with various concentrations of grapefruit seed extract. Thermal and mechanical properties of films varied in grapefruit seed extract films. Furthermore, it was observed that addition of grapefruit seed leads to development of nanoparticles. Authors found that sodium carboxymethyl cellulose facilitates the formation of micelles while glycerides the main component of grape fruit seed extract is encapsulated in the core. These composite films show excellent antibacterial properties due to stable nanoparticles (– 55.26 mV) of grape fruit seed extract. Thus, these films loaded with natural extract can be used in wound healing and other biomedical applications (Koneru *et al.*, 2020). Work of these authors has proven the competency of cellulose based composite hydrogel films as a therapeutic substitute to previous cellulose based dressing, and furthermore, they are easily tuned to achieve specific objectives and deliver the therapeutic moiety at desired area.

ii. Alginate

Alginate is a linear polysaccharide, which is extensively used in wound dressings due to its hemostatic properties (Mogoșanu and Grumezescu, 2014), biocompatibility, non-toxicity, non-immunogenicity, affordability, and high fluid absorption capacity. However, alginate is reported to have poor mechanical properties, which limits its applications. These drawbacks can be overcome by (a) combining it with other suitable polymers to enhance the mechanical properties and modify their release and degradation pattern, (b) secondly, one can enhance its mechanical strength by crosslinking it to form hydrogel. On reviewing literature, we found several authors have developed composite alginate based hydrogel dressings for wound management. For e.g., alginate and pectin based composite hydrogel films were loaded with simvastatin. Here, crosslinking with calcium ions improved the mechanical profile and wound fluid uptake capacity as compared to non-crosslinked films. Non-crosslinked films

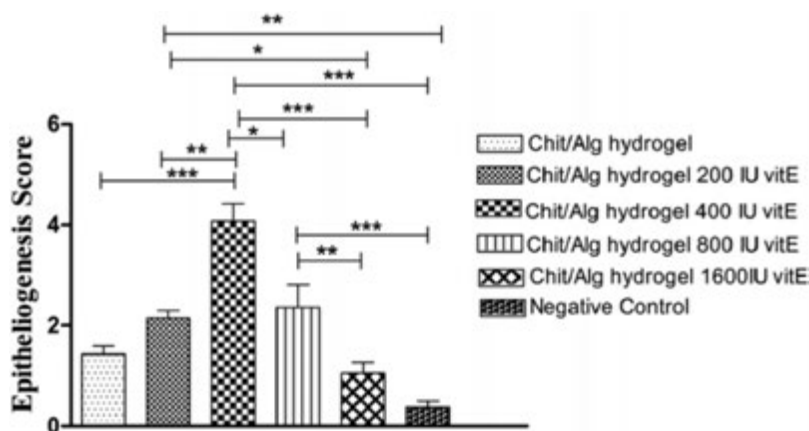


Fig. 9 Epithelialization score of various alginate/chitosan formulation having different concentration of vitamin E. Films with 400 IU of vitamin E responded better than one containing lower or higher concentration of vitamin E. Here, error bar indicated SD ($n = 6$), * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$. Reprinted from Ehterami, A., Salehi, M., Farzamfar, S., *et al.*, 2019. Chitosan/alginate hydrogels containing Alpha-tocopherol for wound healing in rat model. *Journal of Drug Delivery Science and Technology* 51, 204–213, with permission of Elsevier.

released the drug quickly, while crosslinked films released simvastatin in controlled manner and depends on crosslinking density of films. Here, slow and sustained simvastatin delivery, together with higher integrity of the hydrogel dressing is expected to improve wound healing by increasing the duration of drug release and healing process in diabetic wounds (Rezvanian *et al.*, 2017). Although statins are primarily used to lower bad cholesterol in body, but several studies suggest topical use of statins particularly simvastatin can stimulate wound healing as it promotes angiogenesis, lymph angiogenesis, microvascular function, boost immunological response, reduces oxidative stress and infections (Raposo *et al.*, 2016). In another study, alginate was blended with different concentration of Aloe vera (5%, 15% and 25%). Aloe vera had positive influence on the transparency of the films i.e., in dry as well as wet state. Moreover, water absorption capacity of films also increased with contents of Aloe vera. These films were innovative and unique in a sense that both ingredients used for film development also contributed to therapeutic efficacy. For instance, calcium alginate is hemostatic while therapeutic properties of Aloe vera include antibacterial, anti-inflammatory, anti-septic, and fibroblast proliferation activities. So, alginate/Aloe vera hydrogel films can be used as effective wound dressing in dry and exuding wounds (Pereira *et al.*, 2013a).

Alginate/chitosan hydrogel dressing were loaded with various concentrations of α -tocopherol (200–1600 IU) and assessed their efficacy in full-thickness excisional wound model in rats. In this study, researcher combined the two polymers having tissue engineering properties with α -tocopherol, which maintains cell integrity, modulate expression of connective tissue growth factors, and protects wounds against methicillin resistant *S. aureus*. Alginate/chitosan/400 IU α -tocopherol was effective dressings, which showed superior re-epithelization (Fig. 9), hair follicle formation and angiogenesis. This is attributed to antioxidant activity of α -tocopherol that provides protection to cells from oxidative damage and also acts as an important inhibitor of lipid peroxidation and anti-inflammatory agent (Ehterami *et al.*, 2019). At higher doses, wound healing was delayed due to adverse effects of vitamin E as reported previously (Brigelius-Flohé, 2007; Kappus and Diplock, 1992).

Similarly, alginate and chitosan were partially crosslinked with calcium chloride and sodium tripolyphosphate, respectively, and followed by interpolymer complexation. This formulation exhibited 4343.4% swelling, compared to 1612.56% by commercial alginate-based wound dressing (Mndlovu *et al.*, 2019) and thus can serve as potential wound dressings.

iii. Chitosan

Chitosan, a linear polysaccharide, has been revealed as biomaterial for wound management due to its antimicrobial and healing activities. Chitosan is believed to promote the cell migration, fibroblast formation, and cytokines production (Fan *et al.*, 2016). Composite films of chitosan along with other natural polymers have been documented in literature with well-known wound healing potential. Mupirocin loaded chitosan films with or without Aloe vera and sodium alginate and their combination was evaluated for wound healing potential by using rat models. They developed films with and without glutaraldehyde and presence of crosslinker decreased the bioadhesion and swelling. Results showed that the highest wound contraction (98%) was observed with drug loaded chitosan/sodium alginate/Aloe vera composite films on 12th day with superior mechanical properties and thus deemed as effective dressings for all types of wounds (Saleem, 2012). Another group of researcher reported a similar work but they designed the hydrogel films with similar combination i.e., chitosan, sodium alginate and mupirocin but they used carbapol instead of Aloe vera, a biomaterial with wound healing properties. These dressings showed improved mupirocin release, bioadhesion and maximum healing on 10th day in excisional rat model. Histogram revealed fast epidermal regeneration, new blood vessel formation, and granulation when compared with commercial product as shown in Fig. 10 (Okur *et al.*, 2019).

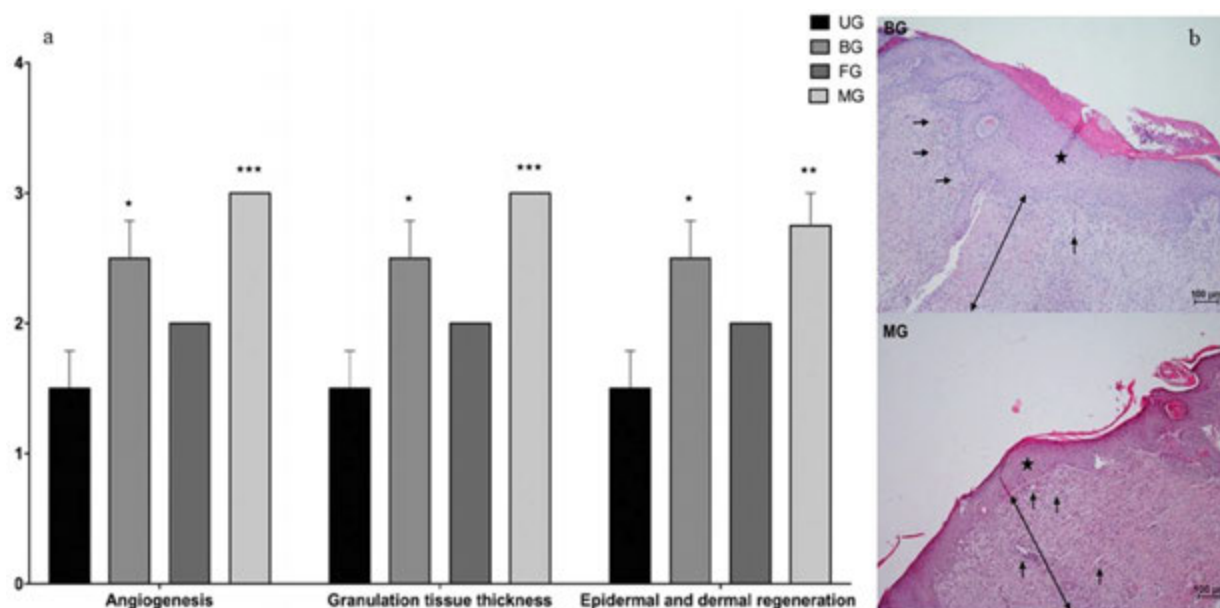


Fig. 10 (a) Histological scores of angiogenesis, granulation tissue thickness, and epidermal/dermal regeneration of untreated (UG), Bactroban® (BG), blank (FG), and mupirocin film (MG) treated groups. (b) Histopathological images of bactroban® and mupirocin film treated groups on 10th day of study after Hemotoxylen and eosin staining, showing better healing of wounds treated with mupirocin film. In this figure ★: Epidermal regeneration, →: Angiogenesis, blood vessels, and ↔: Granulation formation. Adopted from Okur, N.Ü., Hökenek, N., Okur, M.E., *et al.*, 2019. An alternative approach to wound healing field; new composite films from natural polymers for mupirocin dermal delivery. Saudi Pharmaceutical Journal 27, 738–752, with permission of Elsevier.

(b) Proteins and peptides

Several proteins of natural origin such as soya protein, collagen, gelatin and fibrin have applications in wound and burn healing as they stimulate the healing cascade by fibroblast formation, tissue regeneration, and cell proliferation (Mogoşanu and Grumezescu, 2014). For wound healing, numerous studies have been conducted by using natural proteins such as; composite films of soya protein and sago starch were prepared as wound dressings and evaluated in full-thickened wound models in rats. Researcher observed the complete wound closure at 20th day and normal skin like histology in histopathological studies. They also assesses various biochemical parameter like collagen, uronic acid and hexosamine. Higher level of these three parameters indicated the faster wound healing in groups treated with these composite films (Ramnath *et al.*, 2012).

Gelatin is a biopolymer derived from collagen and have numerous applications such as wound dressings, mucoadhesive patches, and other absorbent pads (Roy and Rhim, 2020; Türe, 2019; Fernandes *et al.*, 2018). It is used in tissue engineering and wound healing due to biocompatibility, biodegradability, non-immunogenicity and low cost. Moreover, it contains peptide sequence that recognizes integrin receptors in the cells, which helps in cell adhesion. Gelatin also develops nano-fibrous structure that is important for skin regeneration. Thus, gelatin is able to mimic the extracellular matrix of skin for cellular adhesion, migration and proliferation. Pristine gelatin has low gelling temperature (below 30°C), which hinders its use at the human body temperature. (Zheng *et al.*, 2018). Therefore, it is crosslinked or blended with other polymers to overcome its shortcomings. For instance, gelatin based cross-linked dressing were developed and includes gelatin/alginate and gelatin/hyaluronate and chitosan/hyaluronate to treat full thickened wounds. They loaded silver sulfadiazine in them. Here, gelatin/alginate based sponges with silver sulfadiazine proved to be more effective in healing wounds as compared to other formulations (Choi *et al.*, 2001). Extracellular matrix of skin resembles crosslinked hydrogel network that consists of both polysaccharides and cell-adhesive proteins. Thus to construct a scaffold resembling natural skin, researchers developed methacrylamide-modified gelatin and starch-pentenoate hydrogel films for tissue repair. They also showed gelatin-based hydrogel can be coated with aggrecan (major structural proteoglycan found in the extracellular matrix of cartilage) via physisorption (Van Nieuwenhove *et al.*, 2016). In another study, Li *et al.*, prepared and evaluated composite films as wound dressings by using the combination of gelatin (structural protein of connective tissues) and chitosan (healing promoter and antibacterial). In addition, these films were incorporated with ibuprofen, and were found to be more effective in inhibiting *S. aureus* than *E. coli*. During hemostatic assay these films showed ability to absorb exudate, promoted platelet aggregation, rapid coagulation and clot formation and thus can serve as wound dressings (Li *et al.*, 2017). But these dressings lack any antibacterial properties. So, in more recent study, gelatin/chitosan/silver nanoparticle (Ag NPs), novel composite sponge wound dressing was obtained by crosslinking it with tannic acid. This composite dressing showed good mechanical properties, swelling and more importantly antibacterial effect as compared to the gelatin/chitosan hydrogel dressings. In vivo testing demonstrated, safety, biocompatibility and more importantly reduced the healing time when compared with control, gelatin/chitosan and marketed product called Aquacel® Ag (Ye *et al.*, 2019).

In another study, gelatin-based hydrogels was blended with low content of gellan gum to address the low gelling temperature of gelatin. Electrostatic complexation between gelatin and gellan gum resulted in hydrogel network film at body temperature. To impart antibacterial properties, they loaded tannic acid in hydrogels (Zheng *et al.*, 2018). Türe *et al.*, proposed wound dressing based on gelatin/alginate/hydroxyapatite. They incorporated tetracycline hydrochloride in these composite films, and shown slightly more inhibitory effect against *S. aureus* as compared to *E. coli* the most common opportunistic pathogens of wound area. Moreover, it was observed that swelling ratio and drug release from the films decreased with increasing concentration of alginate and hydroxyapatite but mechanical properties of the films were dependent on the amount of hydroxyapatite and the alginate: gelatin ratio (Türe, 2019). All these studies endorses the use of gelatin as biopolymer for wound dressing.

(c) *Natural gums*

Water soluble natural gums are widely used in pharmaceutical and food industry due to inherent properties such as: high hydration rate, gel forming ability, non-toxicity, wide availability, biodegradability, low antigenicity etc. (Bhardwaj *et al.*, 2000).

i. *Gellan gum*

Gellan gum is anionic, high molecular weight polysaccharide obtained from *Pseudomonas elodea*. Gellan gum is extensively utilized for preparation of composite hydrogel films for various biomedical applications including wound dressings to suppress postoperative adhesions and prevention of scar. It is suggested that gellan gum hydrogels crosslinked by divalent ions possesses excellent mechanical properties, but unfortunately are not stable at physiological pH due to exchange of divalent ions with monovalent ions from biological fluids (Zhang *et al.*, 2020). These limitations are somehow tackled by using its composite. For example, Manda *et al.*, have investigated the potential of gellan gum-hydroxyapatite composites for tissue engineering. In these composites, CaCl_2 and hydroxyapatite reinforced their mechanical properties while gellan gum-hydroxyapatite sponge like hydrogels mimics the organic and inorganic phases of the bone and provide conducive environment for growth of cell at site of injury (Manda-Guiba *et al.*, 2012). Tsai *et al.*, designed the gellan gum-glucosamine patches and loaded with clioquinol via EDC-mediated covalent conjugation to gellan gum/glucosamine. They finally, concluded that these patches are suitable for treatment of early stage cancer and as well as wound dressings after surgery of oral cancer (Tsai *et al.*, 2018). In another study, gellan gum-chitosan hydrogel films were developed by crosslinking it with PEG. They loaded these films with apigenin, a flavonoid rich in various vegetables and plants. Flavonoids are reported to have antioxidant, antibacterial, anti-inflammatory activities and thus can be employed for wound healing application. These films released 96.11% of apigenin in 24 h and during *in vivo* studies apigenin loaded gellan gum-chitosan hydrogel films not only stimulated wound contraction but also significantly enhanced collagen content (Shukla *et al.*, 2016).

ii. *Carrageenan*

Carrageenan belongs to naturally occurring sulphated polysaccharides, and three different types of carrageenan gum are available in market, but mostly kappa carrageenan is employed. κ -carrageenan is widely used as gelling and thickening agent but their films are also investigated as effective wound dressings owing to inherent biocompatibility, it helps in blood coagulation and immune modulation which are helpful attributes for wound healing. Nevertheless, due to poor mechanical properties it is preferred to use it in blended form (Zepon *et al.*, 2019). Literature cites many studies on composite hydrogel films of carrageenan for wound management. For instance, Jaiswal *et al.*, prepared and investigate the carrageenan-chitosan composite films reinforced with grapefruit extract and nanoparticles to be an effective dressing for full-thickened wounds. These composite films showed strong inhibitory effect against *E. coli* and *S. aureus* as well as high healing rate in full-thickened wounds as evident by histopathological images after two weeks of study. It showed thick epidermis, collagen deposition, fibroblast formation and absence of inflammatory cytokines that showed the faster healing rate (Jaiswal *et al.*, 2019). Similarly, carrageenan, agar and chitosan based composite films encapsulated with curcumin have been reported in literature. Uniform distribution of curcumin not only enhanced antibacterial activity but also antioxidant activity of films and thus can be used for food packaging (Roy and Rhim, 2020) as well as wound healing. Apart from above studies literature mentions κ -carrageenan/locust bean gum hydrogel films where authors used cranberry extract (Zepon *et al.*, 2019), to promote wound healing.

iii. *Aloe vera*

Aloe vera is also referred as *Aloe barbadensis* Miller and is widely used in biomedical, pharmaceutical and cosmetic applications. It contains more than seventy-five biologically active constituents and are responsible its antibacterial, antiviral, antifungal, anti-inflammatory, antioxidant and wound healing properties. It contains glucomannan, a water-soluble polysaccharide, which affects fibroblast growth factor from macrophages, which in turn stimulates the activity and proliferation of fibroblast cells. These cells improves collagen production that leads to rearrangement of epithelial tissues (Rahman *et al.*, 2017). Nevertheless, antiseptic, anti-bacterial and anti-inflammatory properties of *Aloe vera* also contributes in healing of wound. Antiseptic ingredients includes salicylic acid, cinnamonic acid, sulfur and lupeol while antioxidant activity results from phenolic and polysaccharide constituents such as mannan, acemannan, glucomannan and flavonoids, flavonols, organic acids (citric acid), etc. (Minjares-Fuentes *et al.*, 2018; Ray *et al.*, 2013). For management of wounds various antibiotics such as minocycline, ofloxacin, gentamycin etc. are used to kill bacterial population responsible for suppressing the wound healing. However, there continues use leads to bacterial resistance. Thus, it would be interesting to use natural biomaterials as wound

dressings with intrinsic antibacterial and wound healing properties such as *Aloe vera* (Pereira *et al.*, 2013a). Moreover, when compared to other polysaccharides, *Aloe vera* has high water swelling efficiency and it can be easily grafted with other polymers due to presence of a large number of functional groups (SaruchiKumar *et al.*, 2018).

So far, several studies have been conducted on use of *Aloe vera* composite hydrogel films as anti-carcinogenic, immune-modulating, anti-ulcer films and as wound dressings for several types of wounds (Pereira *et al.*, 2013a,b; Saleem, 2012). Pereira *et al.*, prepared alginate and *Aloe vera* based composite films by solvent casting-ionotropic gelation method and studied their wound healing properties. They varied the concentration of *Aloe vera* from 5% to 25%, which showed positive influence on transparency and water absorption capacity and thus could be good substitute for wound protection (Pereira *et al.*, 2013b). However, this study lacks the in vivo assessment of developed hydrogel dressing. Similarly, in another study, potato starch/chitosan/*Aloe vera* based hydrogel films were developed with different concentration of *Aloe vera* (10%–50%). *Aloe vera* not only influence thermal stability but also water retention capacity. Presence of *Aloe vera* broadens the scope of films (Bajer *et al.*, 2020) thus can be effectively used for various therapeutic and dressing purposes.

Moreover, alginate/*Aloe vera* hydrogel films obtain by crosslinking with zinc ions (Koga *et al.*, 2020), chitosan/alginate films blended with *Aloe vera* and Ag NPs (Gómez Chabala *et al.*, 2017), alginate/*Aloe vera* hydrogels films obtained by crosslinking with calcium chloride (Pereira *et al.*, 2013c) etc. were found effective in treating wounds. Thus, for wound healing selection of suitable polymers with comparative properties is the major goal of recent research, work of these authors have put a step forward in field of natural polymer based delivery systems for wound management. These systems provide the benefit of using ingredient that not only constitutes dressing matrix but also contributes in prevention of bacterial growth, tissue regeneration and wound repair after it diffuses from composite hydrogel films after its application on wound.

Composite films containing synthetic polymers

Several synthetic polymers have been utilized for synthesis of burn and wound dressings such as polyvinyl alcohol (PVA), polyethylene, polypropylene, polyvinyl chloride (PVC), polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP) etc. due to their good biocompatibility and nontoxic nature (Mogoşanu and Grumezescu, 2014).

i. PVA

It is one of the most frequently utilized synthetic polymer in advanced biomedical field (Kenawy *et al.*, 2014; Kim *et al.*, 2008) for wound management (Zhao *et al.*, 2003), tissue engineering, and drug delivery (Kamoun *et al.*, 2015). However, PVA has limited hydrophilicity, its aqueous solution is transformed to low strength gel (Fathi *et al.*, 2011), which constrain its use as a wound dressing, thus it has been blended with several other synthetic polymers to enhance its mechanical, physical and thermal properties. For e.g., PVA/PVP blended hydrogel films were prepared by crosslinking it with γ -radiation. Wound healing potential of these films was assessed in rat models while comparing it with sterile gauze and Sofra-tulle®. Results showed the better exudate absorption for PVA/PVP blended films than sterile gauze while Sofra-tulle® showed no exudate absorption. Histopathological examination of wounds treated with PVA/PVP blended films showed thick epidermis formation (Razzak and Darwis, 2001). Dextran is Branched poly- α -D-glucosides of microbial origin, is hydrophilic, inert in biological systems, and hardly affects cell integrity. Thus, widely used in pharmaceutical preparations. For instance, Hwang *et al.* developed PVA/dextran hydrogel films which showed low porosity, flat structure, low exudate retention capacity and only showed antibacterial effect after drug loading (Hwang *et al.*, 2010). To overcome such shortcomings first dextran-aldehyde was developed that function as macromolecular cross-linker, and later different concentration of PVA/dextran-aldehyde was crosslinked by freeze-drying. Author claimed that highly porous structure not only absorb large quantity of exudates but also promotes healing. During in vivo studies, PVA/dextran-aldehyde hydrogels have shown promising results when compared with Comfeel® (Zheng *et al.*, 2019). Apart from this study, different authors have prepared PVA/PEG based dressings (Ahmed *et al.*, 2018; Singh *et al.*, 2018; Dutta, 2012) where it was observed that physicochemical and thermal properties of hydrogels were improved after incorporation of PEG.

ii. PVP

PVP is FDA approved non-ionic, hydrophilic, non-toxic, inert, and biocompatible and pH stable polymer. As its structure closely resemble to proteins so it is widely used for biomedical applications and as binder in pharmaceuticals (Liu *et al.*, 2013). PVP blends with other synthetic polymers have been reported in literature as effective wound dressings. PVP/PVA and pomegranate seed nanoparticles based wound dressings were designed by Dogan *et al.*, by freeze thaw method. Findings showed the effectiveness of dressings against *E. coli* and *S. aureus*, thus have potential to be used as wound dressings in infectious wounds (Doğan *et al.*, 2019). Razzak *et al.*, synthesized PVP/PVA blended composite dressings by high energy irradiation method. In their study, authors concluded that these dressings have potential to be used as burn covering dressings as they exhibit good elasticity, effectively absorb exudate and fluids, have good transparency and mechanical properties and act as barrier against microbes (Razzak and Darwis, 2001).

Composite films containing natural and synthetic polymers

Recently the use of combination of natural and synthetic polymers as wound dressings has gained researchers attention as this combination compensates the insufficiencies of thermal stability and mechanical strength of natural polymers. Furthermore, utilization of polymers blend, rather than single polymer; provides the synergistic performance of constituting materials. Following passages will discuss various hydrogel dressing developed by blending natural and synthetic polymers.

Rahmani *et al.*, designed the chitosan, PVA, PVP blended composite films as wound dressing material where chitosan was combined with synthetic polymers to overcome the brittleness, poor physical, mechanical and biological properties of chitosan (Rahmani *et al.*, 2020). Zheng *et al.*, fabricated the dextran/PVA based composite films and these blended composite films were found to be potential dressings for full thickened and cutaneous skin wounds (Zheng *et al.*, 2019). Similarly, several combinations of natural and synthetic polymers have been reported in literature as wound healing materials. For instance, chitosan, PVP and cellulose dressings (Hasan *et al.*, 2017), chitosan, gelatin, PVA based hydrogels for wound healing (Fan *et al.*, 2016), pectin and PVP based membranes (Mishra *et al.*, 2008), xyloglucan and PVA based films for wound healing (Picone *et al.*, 2019), gellan and PVA blends (Sudhamani *et al.*, 2003), chitosan, PEG, PVP dressings (Anjum *et al.*, 2016), gelatin and poly(D,L-lactide-co-glycolide) films (Chung *et al.*, 2016), sodium carboxy methyl cellulose, PEG, PVP wound dressings (Roy *et al.*, 2010), PVA/chitosan hydrogel membranes loaded with ibuprofen- β -cyclodextrins (Morgado *et al.*, 2017). Apart from above studies literature mentions PVA/*Aloe vera* hydrogel films (Hajian *et al.*, 2017), PVP/kappa-carrageenan/PEG hydrogel dressings (De Silva *et al.*, 2011), PVP/carrageenan blend hydrogels with nanosilver (Singh *et al.*, 2015) κ -Carrageenan/PVP/PEG/Ag NPs hydrogel films (Fouda *et al.*, 2015) etc. for wound care management.

Composite hydrogels reinforced with micro and nanocarriers

Micro and nano materials have gained great interest in biomedical application due to their unique and versatile physicochemical properties, controlled shape, specific size characteristics, and modification possibilities. In addition, these particles provide platform for controlled and site specific delivery of drugs, proteins, other bioactive compounds and genes. Metal and metal oxide nanoparticles have antibacterial, anti-fungal, and antiviral activities, while inorganic, semi conductive and magnetic nanoparticles provide the advantage of their use as carrier for hyperthermal, photothermal and photodynamic therapy (Zhao *et al.*, 2015).

Due to aforementioned unique properties, combination of hydrogels and nanoparticles, also known as nanocomposite/hybrid hydrogels have great potential for therapeutic and diagnostic applications. These hybrid hydrogels can be defined as "composite materials incorporated with nano sized materials which are physically or chemically crosslinked in matrix of polymeric network".

Metal/metal oxide nanocomposite wound dressings

Various metal and metal oxide NPs have been investigated due to various therapeutic properties. Among them, Ag NPs have gained more attention due to its broad-spectrum antibacterial activity as well as low toxicity towards human tissues. For example, Ye *et al.*, have designed gelatin/chitosan/Ag nanoparticle composite dressings by crosslinking it with tannic acid. Here, they employed gelatin as matrix agent but it also helped in reduction of AgNO₃ by hydroxyl group of hydroxyproline in gelatin while nonpolar amino acids of gelatin helped to stabilize Ag NPs. Amino group of chitosan, which develops coordinate bonds with Ag⁺, further stabilized these nanoparticles. They observed that gelatin/chitosan/Ag had better mechanical properties when compared with gelatin/chitosan sponges. These composites also showed high inhibitory activity against *E. coli* and *S. aureus* and good water absorption and retention capabilities that kept the wound surface moist for longer duration to promote the wound healing as was evident from histopathological studies that showed development of new skin, absence of inflammatory cytokines and thick epithelia (Ye *et al.*, 2019). Gonzalez *et al.*, prepared wound dressing of PVA/bentonite, PVA/cellulose, PVA/clove extract and PVA/Ag nanocomposite hydrogels by freeze thaw method. They claimed, PVA/Ag NPs and PVA/bentonite showed promising antibacterial activity against *E. coli* and significant vapor transmission rate and high water absorbing capacity, all of these attributes are favorable for wound dressing (Gonzalez *et al.*, 2011). Several other researchers have developed nanocomposites e.g., Ag NPs loaded PVA-acacia gum hydrogels (Juby *et al.*, 2012), hyaluronan, PVA and Ag NPs loaded composites (Zhang *et al.*, 2013), carboxy methyl cellulose and Ag loaded composite hydrogels for biomedical applications (Yadollahi *et al.*, 2015; Hebeish *et al.*, 2013).

Zinc oxide (ZnO) is another important element whose NPs have been intensively investigated for biomedical applications. They have shown promising antibacterial affect against various pathogens after penetration of bacterial cell wall via diffusion. It causes death by disintegrating the bacterial cell membrane and via interaction with various biomolecules in cytoplasm (Siddiqi *et al.*, 2018). Owing to antibacterial properties, they are also finding their way into hydrogel based wound dressings. For instance, chitosan/PVA films were incorporated with different concentration of Tween 80 and ZnO NPs. Presence of these two components affected thermal, mechanical and antibacterial properties of composite hydrogel films. So, authors suggest that these films may be used as effective dressing for wound and burn (Vicentini *et al.*, 2010). Sudheesh *et al.* prepared chitosan and ZnO nanocomposite microporous films with high swelling and vapor transmission rate. They showed excellent antibacterial activity against gram-positive bacteria. During cell attachment and infiltration studies, cells attached with nanocomposite bandages. Histopathological study showed faster re-epithelization and collagen deposition owing to ZnO encapsulation. Authors suggested that these dressings can be used for chronic, diabetic and burn wounds (Sudheesh Kumar *et al.*, 2012). Păunica *et al.*, proposed dextran-collagen-ZnO NPs based nanocomposite films as wound dressings. Under electron microscope, these composite films presented a three-dimensional porous structure with interconnected pores that depends on concentration of dextran and ZnO NPs. Dressings obtained with collagen and dextran presented a more compact structure with smaller pores when compared with one developed with neat collagen. Based upon the rheological, water absorption properties, biological investigations, and degradation studies composite hydrogel based on collagen and dextran with ZnO (50% of collagen weight) were deemed optimum for patients with different wounds. However, this study lacks the in vivo wound healing testing that gives an insight into healing potential and mechanism (Păunica-Panea *et al.*, 2016). In another study, alginate and ZnO NPs (0.05% to 1% w/w) composite bandages were designed for management of infected wounds. These nanocomposites were porous and their porosity decreased in the presence of nanoparticles that could be due to the interaction of alginate with ZnO NPs. Their swelling ratio also decreased with increasing

concentrations of ZnO. These dressings showed excellent antimicrobial activity against strains of *methicillin resistant S. aureus* and other tested bacterial strains. Furthermore, *in vivo* studies showed rapid re-epithelization and keratinocytes migration (Mohandas *et al.*, 2015) to wound site owing to release of zinc ions, which promotes wound healing. Apart from these studies, several other ZnO nanocomposite hydrogel bandages were investigated for wound healing (Luo *et al.*, 2020; Kumar *et al.*, 2013). Thus, addition of metallic nanoparticles to hydrogel wound dressing helps to reduce the bioburden at wound site and providing conducive environment for proliferation of cells.

Carbon based nanocomposite wound dressings

Carbon based nanoparticles have gained popularity in past few decades due to their excellent physicochemical properties. Among them graphene based nanomaterials have been explored as biomaterials for various biomedical applications (Zhao *et al.*, 2015). Fan *et al.*, have developed Ag/graphene composites hydrogels with acrylic acid and N, N'-methylene bisacrylamide as wound dressings. Presence of graphene in hydrogel enhances the tensile strength and elongation break of hydrogel, and thus meets the mechanical strength necessary for wound dressing. These dressing were porous and porosity increased with increasing concentration of Ag NPs, whereas swelling ratio was also highest in formulation with higher quantity of Ag NPs. As porous structures helps to provide sufficient oxygenation, absorbs exudates and maintain moist environment at wound site, thus considered as optimum formulation. These highly porous dressing with high silver content demonstrated good antibacterial activity and promoted healing in artificial wounds (Fan *et al.*, 2014) owing to synergy of Ag NPs and porous graphene structure.

In another study conducted by Usman *et al.*, PVA, starch, graphene oxide and Ag NPs based nanocomposite films were prepared for biomedical applications. Here, also incorporation of graphene oxide enhanced the tensile strength of the nanocomposites films. Furthermore, these films showed significant antibacterial activities against both gram positive and gram negative bacteria. Their antimicrobial activity was in order of PVA-graphene oxide < PVA-Ag < PVA-graphene oxide-Ag < PVA-graphene oxide-Ag-starch films (Usman *et al.*, 2016). Graphene oxide, has reported antimicrobial properties and are strongly affected by its physicochemical properties (sheet size, surface area, purity, structural defects, surface chemical properties, functional groups and degree of oxidation). Furthermore, its antibacterial activity is concentration, time and medium dependent (Cobos *et al.*, 2020). Although synergy of graphene oxide and Ag NPs showed good results but underlying mechanism was not clearly demonstrated. In another study, graphene oxide – silver nanocomposites were developed that showed more toxic effects on *E. coli* than *S. aureus*. The proposed mechanism suggests bactericidal action against the *E. coli* by disrupting bacterial cell wall integrity, whereas it exhibits bacteriostatic effect on the *S. aureus* by inhibiting cell division (Tang *et al.*, 2013).

Other nanoparticles based composite wound dressings

Several other studies have been conducted where numerous other nanoparticles were incorporated into polymeric system for healing of wounds, for example, silver sulfadiazine particles were incorporated into bacterial cellulose based dressings for healing of burn wounds (Wen *et al.*, 2015), poly (ϵ -caprolactone) and gelatin based hydrogel films containing cerium oxide nanoparticles as wound dressings (Zheng *et al.*, 2019). Hsu *et al.*, designed the chitosan-PVA nanocomposite films incorporated with gold nanoparticles and investigated their healing potential. These films showed excellent healing rate with high fibroblast proliferation (Mala *et al.*, 2019). Jaiswal *et al.*, prepared carrageenan and chitosan based hydrogel films encapsulating sulfur nanoparticles and grape fruit seed extract for wound healing purpose. These films showed strong inhibitory activities against *E. coli* and *S. aureus* as well as showed high healing rate in full-thickened wounds as confirmed by significant growth of dermis with high contents of collagen, fibroblasts, sebaceous glands and hair follicles by histopathological studies (Jaiswal *et al.*, 2019). Work of these researchers on use of various organic and inorganic nanoparticles in wound dressings, provide evidence that these nanoparticles gives functional properties to hydrogel based wound dressings and are effective for various dermatological treatments. Ion release from nanoparticles is main healing mechanism where free radical stress in bacteria leads to bacterial killing.

Microparticles based composite wound dressings

Only limited studies report microparticles embedded in hydrogel matrix for wound healing applications. For instance, gellan gum microspheres were prepared with tetracycline hydrochloride and silver sulfadiazine. Later these microparticles were embedded into double crosslinked composite of modified carboxymethyl chitosan and oxidized gellan gum. They double crosslinked the matrix using Schiff base-mediated crosslinking together with ionic crosslinking to overcome instability issues of gellan gum hydrogels at physiological pH (Zhang *et al.*, 2020).

Bilayer hydrogel films

As it has been shown by research that composite films have better physicochemical and thermal stability as compared to single entity based films, similarly, bilayer composite films are gaining preference over single layer films as they make better use of or combine the advantages of unique properties of all substrates (Thu *et al.*, 2012). Term of “bilayer films” was coined by Rivero *et al.*, who developed two hydrocolloids layer, one casted over another, having different constituents in inner and outer layer (Rivero *et al.*, 2009). Bilayer films can be defined as “delivery systems that contain more than one active pharmaceutical ingredient in different layers at same time”. They may provide potential to use two different drugs individually in different layers (Zaman *et al.*, 2018) so as to avoid incompatibility and achieve different release pattern for individual drugs. Now a days, extensive research is carried out over bilayer composite films in biomedical, bioengineering and food technology due to their high mechanical strength,

better optical and gas barrier properties, moisture retaining properties, and ease of preparation (Zhuang *et al.*, 2018). Literature reports use of bilayer films as topical wound dressings, edible films, mucoadhesive films and for food packaging.

Thu *et al.*, designed and synthesized the sodium alginate and gelatin based single as well as bilayer films as wound dressings. Only sodium alginate was used in single layer while in bilayer film either sodium alginate alone or in combination with gelatin was employed for both layers. Here, upper layer was loaded with ibuprofen while lower layer was drug free and acted as rate controlling layer. These bilayer films hydrate slowly and releases the drug in controlled manner as compared to single layer films thus are ideally suited for low suppurating wounds or where slow release of active ingredient over wound is required. It was observed that artificial wound treated with bilayer films healed faster than single layer film (Thu *et al.*, 2012). It's probably because blend of sodium alginate and gelatin reported to show hemostatic effects and enhanced epidermal regeneration (Coviello *et al.*, 2007). In another study, gelatin and chitosan based bilayer films were designed for wound healing purpose. Upper layer of dressing was composed of lactulose crosslinked gelatin to produce a resistant and non-degradable layer that provided mechanical strength while lower layer was composed of citric acid crosslinked gelatin (having high porosity, swelling and degradability) with chitosan that also promotes wound healing. These bilayer films showed above 90% wound contraction in *ex-vivo* wound healing assay (Garcia-Orue *et al.*, 2019). In a more recent study, diclofenac sodium loaded alginate and carboxymethyl cellulose based monolayer and bilayer films were developed by Travisol *et al.*, as wound dressings. They incorporated diclofenac sodium in upper layer of bilayer film to favor slow drug release, as lower drug free layer will act as barrier to mass transfer. Encapsulated drug released over a period of 420 min and 600 min for the mono and bilayer films, respectively. Authors concluded that monolayer film could be utilized for fast pain relief and bilayer film could be effective for wound healing due to controlled drug release (Trevisol *et al.*, 2020). Similarly, many other studies are reported in scientific literature. Chitosan and konjac glucomannan based bilayer films were synthesized as wound dressings (Neto *et al.*, 2019), bilayer membrane consisting of an outer poly(lactic-co-glycolic acid) layer and a lower alginate hydrogel layer, which mimicked the skin epidermis and dermis respectively (Wang *et al.*, 2019), bilayer dressing containing chitosan-oxidized *Bletilla striata* polysaccharide (lower layer) and chitosan-Ag both cross-linked with genipin (upper layer). Here, upper layer provides antibacterial cover while lower layer enhanced the cellular proliferation (Ding *et al.*, 2017), bilayer PLGA/PVA dressing containing stem cell and Ag NPs for wound healing. PLGA layer was developed by electrospinning and contains Ag NPs for antibacterial cover, while stem cells were seeded in PVA hydrogel layer to promote cellular proliferation (Gao *et al.*, 2020).

Hydrogel Based Products in Market

Hydrogels as polymeric dressing are becoming the main commercial target. Several commercial hydrogels have appeared in market as dressing materials. Some of those, with their brand names are discussed below;

(1) *Geliperm*®

Geliperm® sheets are transparent hydrogels with 96% water. These sheets are made up of gellable polysaccharides i.e., agar and polyacrylamide (4%) forming an interwoven molecular network. It is recommended for treatment of acute or chronic wounds involving skin or tissue loss, from burns, dermabrasions, and superficial sores. These highly porous dressings are permeable to gases, water vapors and small protein molecules but impermeable to bacteria, thus provides optimum moist environment at wound site, which is necessary for effective wound healing. Moreover, these dressings also reduce discomfort and local pain.

(2) *Curasol*®

Curasol® gel wound dressings are viscous and clear hydrogels mainly composed of glyceryl polyacrylate and humectants. They are recommended for treatment of low exudating wounds. These highly hydrated dressings provide appropriate moist environment at wound site with mildly absorbent properties. These are fragrance free, non-greasy, and non-inflammatory in nature.

(3) *Tegagel*®

Tegagel® is available in form of sterile fibrous sheet, made up of calcium alginate. These sheets upon contact with solutions of sodium ions, serum or wound exudate, converts to soluble sodium alginate and form a gel on sheet surface. These sheets are recommended for exudating wounds, pressure sores and for diabetic wounds. These dressings provide such environment that facilitates the rapid wound healing and protection against microbial invasion.

(4) *Vigilon*®

Vigilon® hydrogel sheets contain 96% water and are made up of crosslinked polyethylene oxides. These sheets are further strengthened by low-density polyethylene and are recommended for variety of wounds except heavily exudating wounds.

Conclusion

Wound healing is a dynamic process that requires a specific moist environment to encourage earlier wound closure. Variety of dressings from traditional to modern ones are available but selection of specific dressing is crucial for effective wound healing. Traditional dressings may reinjure the wound, as well as are permeable to bacteria, thus, researcher are working on modern dressings such as hydrogel films which effectively inhibits growth of microorganisms and promote healing cascade by stimulating

fibroblast formation. However, composite films were found more effective and suitable for wound care management and includes composite films developed using blend of natural or synthetic polymers, bilayer films, films blended with micro and nanoparticles. It is evident from studies that development of composite films, overcomes shortcomings of single polymeric system by improving the mechanical, physicochemical, thermal stability, and antibacterial of films. Furthermore, incorporation of micro or nanoparticles, or different bioactive materials in different layers of films has proven as an innovative mean to improve robustness and impart multiple functionalities to hydrogel dressings.

However, besides the major progress in composite films, there are still some challenges that must be overcome before their clinical use. As nanoparticles provide large surface area so hydrophobic nanoparticles may have embedded or form aggregates in polymeric matrix so their homogeneity in polymeric matrix is still a matter of concern. Secondly, despite limited in vivo studies their long term toxicological and tissue compatibilities studies are needed before marketing.

References

- Adamian, A., Dobysh, S., Kilimchuk, L., Shandurenko, I., Chekmareva, I., 2004. Development of new biologically active dressings and methodology of their use. *Khirurgia*, 10–14.
- Ahmed, A.S., Mandal, U.K., Taher, M., Susanti, D., Jaffri, J.M., 2018. PVA-PEG physically cross-linked hydrogel film as a wound dressing: experimental design and optimization. *Pharmaceutical Development and Technology* 23, 751–760.
- Ahmed, E.M., 2015. Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research* 6, 105–121.
- Akhtar, M.F., Hanif, M., Ranjha, N.M., 2016. Methods of synthesis of hydrogels... A review. *Saudi Pharmaceutical Journal* 24, 554–559.
- Alavi, T., Rezvanian, M., Ahmad, N., Mohamad, N., Ng, S.-F., 2019. Pluronic-F127 composite film loaded with erythromycin for wound application: formulation, physicochemical and in vitro evaluations. *Drug Delivery and Translational Research* 9, 508–519.
- Ali, A., Ahmed, S., 2018. Recent advances in edible polymer based hydrogels as a sustainable alternative to conventional polymers. *Journal of Agricultural and Food Chemistry* 66, 6940–6967.
- Altioek, D., Altioek, E., Tihminlioglu, F., 2010. Physical, antibacterial and antioxidant properties of chitosan films incorporated with thyme oil for potential wound healing applications. *Journal of Materials Science: Materials in Medicine* 21, 2227–2236.
- Anjum, S., Arora, A., Alam, M., Gupta, B., 2016. Development of antimicrobial and scar preventive chitosan hydrogel wound dressings. *International Journal of Pharmaceutics* 508, 92–101.
- Bajer, D., Janczak, K., Bajer, K., 2020. Novel starch/chitosan/aloe vera composites as promising biopackaging materials. *Journal of Polymers and the Environment* 28, 1021–1039.
- Bhardwaj, T.R., Kanwar, M., Lal, R., Gupta, A., 2000. Natural gums and modified natural gums as sustained-release carriers. *Drug Development and Industrial Pharmacy* 26, 1025–1038.
- Bhowmik, D., Gopinath, H., Kumar, B.P., Duraivel, S., Kumar, K.S., 2012. Recent advances in novel topical drug delivery system. *The Pharma Innovation* 1.12.
- Boateng, J.S., Matthews, K.H., Stevens, H.N., Eccleston, G.M., 2008. Wound healing dressings and drug delivery systems: a review. *Journal of Pharmaceutical Sciences* 97, 2892–2923.
- Brigelius-Flohé, R., 2007. Adverse effects of vitamin E by induction of drug metabolism. *Genes & Nutrition* 2, 249–256.
- Bruce, J., Wong, I., 2001. Parenteral drug administration errors by nursing staff on an acute medical admissions ward during day duty. *Drug Safety* 24, 855–862.
- Choi, Y.S., Lee, S., Hong, S.R., *et al.*, 2001. Studies on gelatin-based sponges. Part III: A comparative study of cross-linked gelatin/alginate, gelatin/hyaluronate and chitosan/hyaluronate sponges and their application as a wound dressing in full-thickness skin defect of rat. *Journal of Materials Science: Materials in Medicine* 12, 67–73.
- Chung, T.-W., Chou, T.-H., Wu, K.-Y., 2016. Gelatin/PLGA hydrogel films and their delivery of hydrophobic drugs. *Journal of the Taiwan Institute of Chemical Engineers* 60, 8–14.
- Cobos, M., De-La-Pinta, I., Quindós, G., 2020. Synthesis, physical, mechanical and antibacterial properties of nanocomposites based on poly(vinyl alcohol)/graphene oxide-silver nanoparticles. *Polymers* 12.
- Coviello, T., Matricardi, P., Marianecci, C., Alhaique, F., 2007. Polysaccharide hydrogels for modified release formulations. *Journal of Controlled Release* 119, 5–24.
- De Silva, D.A., Hettiarachchi, B.U., Nayanajith, L., Milani, M.Y., Motha, J., 2011. Development of a PVP/kappa-carrageenan/PEG hydrogel dressing for wound healing applications in Sri Lanka. *Journal of the National Science Foundation of Sri Lanka* 39, 25–33.
- Ding, L., Shan, X., Zhao, X., *et al.*, 2017. Spongy bilayer dressing composed of chitosan–Ag nanoparticles and chitosan–Bletila striata polysaccharide for wound healing applications. *Carbohydrate Polymers* 157, 1538–1547.
- Doğan, E.E., Tokcan, P., Diken, M.E., *et al.*, 2019. Synthesis, characterization and some biological properties of PVA/PVP/PN hydrogel nanocomposites: Antibacterial and biocompatibility. *Advances in Materials Science* 19, 32–45.
- Dumville, J.C., O'Meara, S., Deshpande, S., Speak, K., 2013. Hydrogel dressings for healing diabetic foot ulcers. *Cochrane Database of Systematic Reviews* 2013 (7), CD009101. doi:10.1002/14651858.CD009101.pub3.
- Dutta, J., 2012. Synthesis and characterization of γ -irradiated PVA/PEG/CaCl₂ hydrogel for wound dressing. *Journal of the American Chemical Society* 2, 6–11.
- Edwards, J.V., Yager, D.R., Cohen, I.K., *et al.*, 2001. Modified cotton gauze dressings that selectively absorb neutrophil elastase activity in solution. *Wound Repair and Regeneration* 9, 50–58.
- Ehterami, A., Salehi, M., Farzamfar, S., *et al.*, 2019. Chitosan/alginate hydrogels containing Alpha-tocopherol for wound healing in rat model. *Journal of Drug Delivery Science and Technology* 51, 204–213.
- Ejaz, M., Arfat, Y.A., Mulla, M., Ahmed, J., 2018. Zinc oxide nanorods/clove essential oil incorporated Type B gelatin composite films and its applicability for shrimp packaging. *Food Packaging and Shelf Life* 15, 113–121.
- Fan, L., Yang, H., Yang, J., Peng, M., Hu, J., 2016. Preparation and characterization of chitosan/gelatin/PVA hydrogel for wound dressings. *Carbohydrate Polymers* 146, 427–434.
- Fan, Z., Liu, B., Wang, J., *et al.*, 2014. A novel wound dressing based on Ag/graphene polymer hydrogel: Effectively kill bacteria and accelerate wound healing. *Advanced Functional Materials* 24, 3933–3943.
- Fathi, E., Atiyabi, N., Imani, M., Alinejad, Z., 2011. Physically crosslinked polyvinyl alcohol–dextran blend xerogels: Morphology and thermal behavior. *Carbohydrate Polymers* 84, 145–152.
- Fernandes, F.P., Fortes, A.C., Da Cruz Fonseca, S.G., Breikreutz, J., Ferraz, H.G., 2018. Manufacture and characterization of mucoadhesive buccal films based on pectin and gellan gum containing triamcinolone acetonide. *International Journal of Polymer Science* 2018.
- Fouda, M.M.G., El-Aassar, M.R., El Fawal, G.F., *et al.*, 2015. *k*-Carrageenan/poly vinyl pyrrolidone/polyethylene glycol/silver nanoparticles film for biomedical application. *International journal of biological macromolecules* 74, 179–184.
- Gaharwar, A.K., Peppas, N.A., Khademhosseini, A., 2014. Nanocomposite hydrogels for biomedical applications. *Biotechnology and Bioengineering* 111, 441–453.

- Gao, T., Tian, C., Ma, Z., *et al.*, 2020. Stem cell seeded and silver nanoparticles loaded bilayer PLGA/PVA dressings for wound healing. *Macromolecular Bioscience* 20 (10), 2000141.
- García-Orue, I., Santos-Vizcaino, E., Etxabide, A., *et al.*, 2019. Development of bioinspired gelatin and gelatin/chitosan bilayer hydrofilms for wound healing. *Pharmaceutics* 11, 314.
- Gómez Chabala, L.F., Cuartas, C.E.E., López, M.E.L., 2017. Release behavior and antibacterial activity of chitosan/alginate blends with aloe vera and silver nanoparticles. *Marine Drugs* 15.
- Gonzalez, J.S., Maiolo, A.S., Ponce, A.G., Alvarez, V.A., 2011. Composites based on poly (vinyl alcohol) hydrogels for wound dressing. In: *Proceedings of the XVIII The Argentine Congress of Bioengineering and Clinical Engineering Conference VII, SABI*.
- Grampurohit, N., Ravikumar, P., Mallya, R., 2011. Microemulsions for topical use – A review. *Indian Journal of Pharmaceutical Education and Research* 45, 100–107.
- Hajian, M., Mahmoodi, M., Imani, R., 2017. In vitro assessment of poly (vinyl alcohol) film incorporating aloe vera for potential application as a wound dressing. *Journal of Macromolecular Science, Part B* 56, 435–450.
- Hasan, A., Waibhaw, G., Tiwari, S., *et al.*, 2017. Fabrication and characterization of chitosan, polyvinylpyrrolidone, and cellulose nanowhiskers nanocomposite films for wound healing drug delivery application. *Journal of Biomedical Materials Research Part A* 105, 2391–2404.
- Hebeish, A., Hashem, M., El-Hady, M.A., Sharaf, S., 2013. Development of CMC hydrogels loaded with silver nano-particles for medical applications. *Carbohydrate Polymers* 92, 407–413.
- Hoare, T.R., Kohane, D.S., 2008. Hydrogels in drug delivery: Progress and challenges. *Polymer* 49, 1993–2007.
- Hopewell, J., 1990. The skin: its structure and response to ionizing radiation. *International Journal of Radiation Biology* 57, 751–773.
- Huang, S., Fu, X., 2010. Naturally derived materials-based cell and drug delivery systems in skin regeneration. *Journal of Controlled Release* 142, 149–159.
- Hwang, M.-R., Kim, J.O., Lee, J.H., *et al.*, 2010. Gentamicin-loaded wound dressing with polyvinyl alcohol/dextran hydrogel: Gel characterization and in vivo healing evaluation. *AAPS PharmSciTech* 11, 1092–1103.
- Inngjerdengen, K., Nergård, C.S., Diallo, D., Mounkoro, P.P., Paulsen, B.S., 2004. An ethnopharmacological survey of plants used for wound healing in Dogonland, Mali, West Africa. *Journal of Ethnopharmacology* 92, 233–244.
- Jaiswal, L., Shankar, S., Rhim, J.-W., 2019. Carrageenan-based functional hydrogel film reinforced with sulfur nanoparticles and grapefruit seed extract for wound healing application. *Carbohydrate Polymers* 224, 115191.
- Juby, K., Dwivedi, C., Kumar, M., *et al.*, 2012. Silver nanoparticle-loaded PVA/gum acacia hydrogel: Synthesis, characterization and antibacterial study. *Carbohydrate Polymers* 89, 906–913.
- Kabir, S.M.F., Sikdar, P.P., Haque, B., *et al.*, 2018. Cellulose-based hydrogel materials: Chemistry, properties and their prospective applications. *Progress in Biomaterials* 7, 153–174.
- Kamoun, E.A., Kenawy, E.-R.S., Chen, X., 2017. A review on polymeric hydrogel membranes for wound dressing applications: pva-based hydrogel dressings. *Journal of Advanced Research* 8, 217–233.
- Kamoun, E.A., Chen, X., Eldin, M.S.M., Kenawy, E.-R.S., 2015. Crosslinked poly (vinyl alcohol) hydrogels for wound dressing applications: A review of remarkably blended polymers. *Arabian Journal of Chemistry* 8, 1–14.
- Kappus, H., Diplock, A.T., 1992. Tolerance and safety of vitamin E: A toxicological position report. *Free Radical Biology and Medicine* 13, 55–74.
- Kenawy, E.-R., Eldin, M.S.M., El-Meligy, M.A., 2014. Physically crosslinked poly (vinyl alcohol)-hydroxyethyl starch blend hydrogel membranes: Synthesis and characterization for biomedical applications. *Arabian Journal of Chemistry* 7, 372–380.
- Khamrai, M., Banerjee, S.L., Paul, S., Samanta, S., Kundu, P.P., 2019. Curcumin entrapped gelatin/ionically modified bacterial cellulose based self-healable hydrogel film: An eco-friendly sustainable synthesis method of wound healing patch. *International Journal of Biological Macromolecules* 122, 940–953.
- Kim, J.O., Park, J.K., Kim, J.H., *et al.*, 2008. Development of polyvinyl alcohol–sodium alginate gel-matrix-based wound dressing system containing nitrofurazone. *International Journal of Pharmaceutics* 359, 79–86.
- Koga, A.Y., Felix, J.C., Silvestre, R.G.M., *et al.*, 2020. Evaluation of wound healing effect of alginate film containing Aloe vera gel and cross-linked with zinc chloride. *Acta Cirurgica Brasileira* 35, e202000507.
- Kokabi, M., Sirousazar, M., Hassan, Z.M., 2007. PVA–clay nanocomposite hydrogels for wound dressing. *European Polymer Journal* 43, 773–781.
- Koneru, A., Dharmalingam, K., Anandalakshmi, R., 2020. Cellulose based nanocomposite hydrogel films consisting of sodium carboxymethylcellulose–grapefruit seed extract nanoparticles for potential wound healing applications. *International Journal of Biological Macromolecules* 148, 833–842.
- Kuijpers, A., Van Wachem, P., Van Luyn, M., *et al.*, 2000. In vivo and in vitro release of lysozyme from cross-linked gelatin hydrogels: A model system for the delivery of antibacterial proteins from prosthetic heart valves. *Journal of Controlled Release* 67, 323–336.
- Kumar, S., Lakshmanan, V.-K., Raj, M., *et al.*, 2013. Evaluation of wound healing potential of β -chitin hydrogel/nano zinc oxide composite bandage. *Pharmaceutical Research* 30, 523–537.
- Künzler, J.F., 2002. Chapter – 2. Hydrogels. *Encyclopedia of Polymer Science and Technology*.
- Li, H., Cheng, F., Gao, S., *et al.*, 2017. Preparation, characterization, antibacterial properties, and hemostatic evaluation of ibuprofen-loaded chitosan/gelatin composite films. *Journal of Applied Polymer Science* 134, 45441.
- Liu, L., Fishman, M.L., Kost, J., Hicks, K.B., 2003. Pectin-based systems for colon-specific drug delivery via oral route. *Biomaterials* 24, 3333–3343.
- Liu, X., Xu, Y., Wu, Z., Chen, H., 2013. Poly (N-vinylpyrrolidone)-modified surfaces for biomedical applications. *Macromolecular Bioscience* 13, 147–154.
- Liu, Y., Wang, X., Yang, F., Yang, X., 2008. Excellent antimicrobial properties of mesoporous anatase TiO₂ and Ag/TiO₂ composite films. *Microporous and Mesoporous Materials* 114, 431–439.
- Luo, Z., Liu, J., Lin, H., 2020. In situ fabrication of nano ZnO/BCM biocomposite based on MA modified bacterial cellulose membrane for antibacterial and wound healing. *International Journal of Nanomedicine* 15, 1–15.
- Mala, R., Rani, M.J., Prasath, N.H., Celsia, A.R., 2019. Nano composite material of chitosan for wound healing: A review. *AIP Conference Proceedings* 2105, 020013.
- Mali, K.K., Dhawale, S.C., Dias, R.J., 2017. Synthesis and characterization of hydrogel films of carboxymethyl tamarind gum using citric acid. *International Journal of Biological Macromolecules* 105, 463–470.
- Manda-Guiba, G., Oliveira, M.B., Mano, J., *et al.*, 2012. Gellan gum: Hydroxyapatite composite hydrogels for bone tissue engineering. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 108 (12).
- Mateescu, A., Wang, Y., Dostalek, J., Jonas, U., 2012. Thin hydrogel films for optical biosensor applications. *Membranes* 2, 40–69.
- Mazzitelli, S., Pagano, C., Giusepponi, D., Nastruzzi, C., Peroli, L., 2013. Hydrogel blends with adjustable properties as patches for transdermal delivery. *International Journal of Pharmaceutics* 454, 47–57.
- Metcalfe, A.D., Ferguson, M.W., 2007. Bioengineering skin using mechanisms of regeneration and repair. *Biomaterials* 28, 5100–5113.
- Minjares-Fuentes, R., Femenia, A., Comas-Serra, F., Rodríguez-González, V.M., 2018. Compositional and structural features of the main bioactive polysaccharides present in the aloe vera plant. *Journal of AOAC International* 101, 1711–1719.
- Mishra, R.K., Datt, M., Banthia, A.K., 2008. Synthesis and characterization of pectin/PVP hydrogel membranes for drug delivery system. *AAPS PharmSciTech* 9, 395–403.
- Mndlovu, H., Du Toit, L.C., Kumar, P., *et al.*, 2019. Development of a fluid-absorptive alginate-chitosan bioplatfrom for potential application as a wound dressing. *Carbohydrate Polymers* 222, 114988.
- Mogoşanu, G.D., Grumezescu, A.M., 2014. Natural and synthetic polymers for wounds and burns dressing. *International Journal of Pharmaceutics* 463, 127–136.

- Mohandas, A., Sudheesh Kumar, P., Raja, B., Lakshmanan, V.-K., Jayakumar, R., 2015. Exploration of alginate hydrogel/nano zinc oxide composite bandages for infected wounds. *International Journal of Nanomedicine* 10, 53.
- Morgado, P.I., Miguel, S.P., Correia, I.J., Aguiar-Ricardo, A., 2017. Ibuprofen loaded PVA/chitosan membranes: A highly efficient strategy towards an improved skin wound healing. *Carbohydrate Polymers* 159, 136–145.
- Moura, L.I., Dias, A.M., Carvalho, E., De Sousa, H.C., 2013. Recent advances on the development of wound dressings for diabetic foot ulcer treatment—A review. *Acta Biomaterialia* 9, 7093–7114.
- Neto, R.J.G., Genevro, G.M., De Almeida Paulo, L., *et al.*, 2019. Characterization and in vitro evaluation of chitosan/konjac glucomannan bilayer film as a wound dressing. *Carbohydrate Polymers* 212, 59–66.
- Okur, N.Ü., Hökenek, N., Okur, M.E., *et al.*, 2019. An alternative approach to wound healing field; new composite films from natural polymers for mupirocin dermal delivery. *Saudi Pharmaceutical Journal* 27, 738–752.
- Păunica-Panea, G., Fica, A., Marin, M.M., *et al.*, 2016. New collagen-dextran-zinc oxide composites for wound dressing. *Journal of Nanomaterials* 2016.
- Pereira, R., Carvalho, A., Vaz, D.C., *et al.*, 2013a. Development of novel alginate based hydrogel films for wound healing applications. *International Journal of Biological Macromolecules* 52, 221–230.
- Pereira, R., Mendes, A., Bártolo, P., 2013b. Alginate/Aloe vera hydrogel films for biomedical applications. *Procedia CIRP* 5, 210–215.
- Pereira, R., Mendes, A., Bártolo, P., 2013c. Novel alginate/Aloe vera hydrogel blends as wound dressings for the treatment of several types of wounds. *Chemical Engineering Transactions* 32, 1009–1014.
- Picone, P., Sabatino, M.A., Ajovalasit, A., *et al.*, 2019. Biocompatibility, hemocompatibility and antimicrobial properties of xyloglucan-based hydrogel film for wound healing application. *International Journal of Biological Macromolecules* 121, 784–795.
- Pinho, E., Soares, G., 2018. Functionalization of cotton cellulose for improved wound healing. *Journal of Materials Chemistry B* 6, 1887–1898.
- Prausnitz, M.R., Langer, R., 2008. Transdermal drug delivery. *Nature Biotechnology* 26, 1261.
- Purna, S.K., Babu, M., 2000. Collagen based dressings—A review. In: *Burns: Journal of the International Society for Burn Injuries*, 26, 54.
- Queen, D., Orsted, H., Sanada, H., Sussman, G., 2004. A dressing history. *International Wound Journal* 1, 59–77.
- Rahman, S., Carter, P., Bhattarai, N., 2017. Aloe vera for tissue engineering applications. *Journal of Functional Biomaterials* 8, 6.
- Rahmani, H., Najafi, S.H.M., Ashori, A., *et al.*, 2020. Preparation of chitosan-based composites with urethane cross linkage and evaluation of their properties for using as wound healing dressing. *Carbohydrate Polymers* 230, 115606.
- Ramnath, V., Sekar, S., Sankar, S., Sastry, T., Mandal, A., 2012. In vivo evaluation of composite wound dressing material containing soya protein and sago starch. *International Journal of Pharmacy and Pharmaceutical Sciences* 4, 414–419.
- Raposio, E., Libondi, G., Bertozzi, N., Grignaffini, E., Grieco, M.P., 2016. Effects of topic simvastatin for the treatment of chronic vascular cutaneous ulcers: A pilot study. *The Journal of the American College of Clinical Wound Specialists* 7, 13–18.
- Rathbone, M.J., Drummond, B.K., Tucker, I.G., 1994. The oral cavity as a site for systemic drug delivery. *Advanced Drug Delivery Reviews* 13, 1–22.
- Ray, A., Gupta, S.D., Ghosh, S., 2013. Evaluation of anti-oxidative activity and UV absorption potential of the extracts of Aloe vera L. gel from different growth periods of plants. *Industrial Crops and Products* 49, 712–719.
- Ray, D., Gils, P.S., Mohanta, G.P., Manavalan, R., Sahoo, P.K., 2010. Comparative delivery of diltiazem hydrochloride through synthesized polymer: hydrogel and hydrogel microspheres. *Journal of Applied Polymer Science* 116, 959–968.
- Razzak, M.T., Darwis, D., 2001. Irradiation of polyvinyl alcohol and polyvinyl pyrrolidone blended hydrogel for wound dressing. *Radiation Physics and Chemistry* 62, 107–113.
- Reinke, J., Sorg, H., 2012. Wound repair and regeneration. *European Surgical Research* 49, 35–43.
- Rezvani, M., Ahmad, N., Amin, M.C.I.M., Ng, S.-F., 2017. Optimization, characterization, and in vitro assessment of alginate-pectin ionic cross-linked hydrogel film for wound dressing applications. *International Journal of Biological Macromolecules* 97, 131–140.
- Rivero, S., García, M., Pinotti, A., 2009. Composite and bi-layer films based on gelatin and chitosan. *Journal of Food Engineering* 90, 531–539.
- Roy, N., Saha, N., Kitano, T., Saha, P., 2010. Development and characterization of novel medicated hydrogels for wound dressing. *Soft Materials* 8, 130–148.
- Roy, S., Rhim, J.-W., 2020. Preparation of carbohydrate-based functional composite films incorporated with curcumin. *Food Hydrocolloids* 98, 105302.
- Saleem, M., 2012. Preparation and evaluation of mupirocin loaded polymer composite films. *Journal of Drug Delivery and Therapeutics* 2 (3).
- Sarheed, O., Ahmed, A., Shouqair, D., Boateng, J., 2016. Antimicrobial dressings for improving wound healing. In *Wound Healing-New insights into Ancient Challenges*. InTech.
- SaruchiKumar, V., Rehani, V., Kaith, B.S., 2018. Microwave-assisted synthesis of biodegradable interpenetrating polymer network of Aloe vera–poly(acrylic acid-co-acrylamide) for removal of malachite green dye: Equilibrium, kinetics and thermodynamic studies. *Iranian Polymer Journal* 27, 913–926.
- Seliktar, D., 2012. Designing cell-compatible hydrogels for biomedical applications. *Science* 336, 1124–1128.
- Shukla, R., Kashaw, S.K., Jain, A.P., Lodhi, S., 2016. Fabrication of apigenin loaded gellan gum–chitosan hydrogels (GGCH-HGs) for effective diabetic wound healing. *International Journal of Biological Macromolecules* 91, 1110–1119.
- Siddiqi, K.S., Ur Rahman, A., Tajuddin Husen, A., 2018. Properties of zinc oxide nanoparticles and their activity against microbes. *Nanoscale Research Letters* 13, 141.
- Singh, D., Singh, A., Singh, R., 2015. Polyvinyl pyrrolidone/carrageenan blend hydrogels with nanosilver prepared by gamma radiation for use as an antimicrobial wound dressing. *Journal of Biomaterials Science, Polymer Edition* 26, 1269–1285.
- Singh, P., Bharati, D.C., Gupta, P., Saroj, A., 2018. Vibrational, thermal and ion transport properties of PVA-PVP-PEG-MeSO₄Na based polymer blend electrolyte films. *Journal of Non-Crystalline Solids* 494, 21–30.
- Sudhamani, S., Prasad, M., Sankar, K.U., 2003. DSC and FTIR studies on gellan and polyvinyl alcohol (PVA) blend films. *Food Hydrocolloids* 17, 245–250.
- Sudheesh Kumar, P., Lakshmanan, V.-K., Anilkumar, T., *et al.*, 2012. Flexible and microporous chitosan hydrogel/nano ZnO composite bandages for wound dressing: In vitro and in vivo evaluation. *ACS Applied Materials & Interfaces* 4, 2618–2629.
- Takigami, M., Amada, H., Nagasawa, N., *et al.*, 2007. Preparation and properties of CMC gel. *Transactions-Materials Research Society of Japan* 32, 713.
- Tang, J., Chen, Q., Xu, L., *et al.*, 2013. Graphene oxide-silver nanocomposite as a highly effective antibacterial agent with species-specific mechanisms. *ACS Applied Materials & Interfaces* 5, 3867–3874.
- Thomas, S., 2000. Alginate dressings in surgery and wound management—Part 1. *Journal of Wound Care* 9, 56–60.
- Thu, H.-E., Zulfakar, M.H., Ng, S.-F., 2012. Alginate based bilayer hydrocolloid films as potential slow-release modern wound dressing. *International Journal of Pharmaceutics* 434, 375–383.
- Tiwari, G., Tiwari, R., Sriwastawa, B., *et al.*, 2012. Drug delivery systems: An updated review. *International Journal of Pharmaceutical Investigation* 2.
- Trevisol, T.C., Scartazzini, L., Valerio, A., *et al.*, 2020. Dicarboxy/carboxymethyl cellulose mono and bilayer films for wound dressing applications. *Cellulose* 27, 6629–6642. doi:10.1007/s10570-020-03217-3.
- Tsai, W., Tsai, H., Wong, Y., *et al.*, 2018. Preparation and characterization of gellan gum/glucosamine/clioquinol film as oral cancer treatment patch. *Materials Science and Engineering: C* 82, 317–322.
- Türe, H., 2019. Characterization of hydroxyapatite-containing alginate–gelatin composite films as a potential wound dressing. *International Journal of Biological Macromolecules* 123, 878–888.
- Uliniuc, A., Hamaide, T., Popa, M., Băcăiță, S., 2013. Modified starch-based hydrogels cross-linked with citric acid and their use as drug delivery systems for levofloxacin. *Soft Materials* 11, 483–493.

- Ullah, F., Othman, M.B.H., Javed, F., Ahmad, Z., Akil, H.M., 2015. Classification, processing and application of hydrogels: A review. *Materials Science and Engineering: C* 57, 414–433.
- Usman, A., Hussain, Z., Riaz, A., Khan, A.N., 2016. Enhanced mechanical, thermal and antimicrobial properties of poly (vinyl alcohol)/graphene oxide/starch/silver nanocomposites films. *Carbohydrate Polymers* 153, 592–599.
- Van Nieuwenhove, I., Salamon, A., Peters, K., *et al.*, 2016. Gelatin-and starch-based hydrogels. Part A: Hydrogel development, characterization and coating. *Carbohydrate Polymers* 152, 129–139.
- Van Rijswijk, L., 2006. Ingredient-based wound dressing classification: A paradigm that is passe and in need of replacement. *Journal of Wound Care* 15, 11–14.
- Varaprasad, K., Raghavendra, G.M., Jayaramudu, T., Yallapu, M.M., Sadiku, R., 2017. A mini review on hydrogels classification and recent developments in miscellaneous applications. *Materials Science and Engineering: C* 79, 958–971.
- Vicentini, D.S., Smania Jr, A., Laranjeira, M.C., 2010. Chitosan/poly (vinyl alcohol) films containing ZnO nanoparticles and plasticizers. *Materials Science and Engineering: C* 30, 503–508.
- Wang, S., Xiong, Y., Chen, J., *et al.*, 2019. Three dimensional printing bilayer membrane scaffold promotes wound healing. *Frontiers in Bioengineering and Biotechnology* 7.
- Wen, X., Zheng, Y., Wu, J., *et al.*, 2015. In vitro and in vivo investigation of bacterial cellulose dressing containing uniform silver sulfadiazine nanoparticles for burn wound healing. *Progress in Natural Science: Materials International* 25, 197–203.
- Yadollahi, M., Namazi, H., Aghazadeh, M., 2015. Antibacterial carboxymethyl cellulose/Ag nanocomposite hydrogels cross-linked with layered double hydroxides. *International Journal of Biological Macromolecules* 79, 269–277.
- Ye, E., Loh, X.J., 2013. Polymeric hydrogels and nanoparticles: A merging and emerging field. *Australian Journal of Chemistry* 66, 997–1007.
- Ye, H., Cheng, J., Yu, K., 2019. In situ reduction of silver nanoparticles by gelatin to obtain porous silver nanoparticle/chitosan composites with enhanced antimicrobial and wound-healing activity. *International Journal of Biological Macromolecules* 121, 633–642.
- Zaman, M., Hanif, M., Shaheryar, Z.A., 2018. Development of tizanidine HCl-meloxicam loaded mucoadhesive buccal films: In-vitro and in-vivo evaluation. *PLoS One* 13.
- Zepon, K.M., Martins, M.M., Marques, M.S., *et al.*, 2019. Smart wound dressing based on κ -carrageenan/locust bean gum/cranberry extract for monitoring bacterial infections. *Carbohydrate Polymers* 206, 362–370.
- Zhai, M., Yoshii, F., Kume, T., Hashim, K., 2002. Syntheses of PVA/starch grafted hydrogels by irradiation. *Carbohydrate Polymers* 50, 295–303.
- Zhang, F., Wu, J., Kang, D., Zhang, H., 2013. Development of a complex hydrogel of hyaluronan and PVA embedded with silver nanoparticles and its facile studies on *Escherichia coli*. *Journal of Biomaterials Science, Polymer Edition* 24, 1410–1425.
- Zhang, X., Pan, Y., Li, S., *et al.*, 2020. Doubly crosslinked biodegradable hydrogels based on gellan gum and chitosan for drug delivery and wound dressing. *International Journal of Biological Macromolecules* 164, 2204–2214.
- Zhao, F., Yao, D., Guo, R., *et al.*, 2015. Composites of polymer hydrogels and nanoparticulate systems for biomedical and pharmaceutical applications. *Nanomaterials* 5, 2054–2130.
- Zhao, L., Mitomo, H., Zhai, M., *et al.*, 2003. Synthesis of antibacterial PVA/CM-chitosan blend hydrogels with electron beam irradiation. *Carbohydrate Polymers* 53, 439–446.
- Zheng, C., Liu, C., Chen, H., *et al.*, 2019. Effective wound dressing based on Poly (vinyl alcohol)/Dextran-aldehyde composite hydrogel. *International Journal of Biological Macromolecules* 132, 1098–1105.
- Zheng, Y., Liang, Y., Zhang, D., *et al.*, 2018. Gelatin-based hydrogels blended with gellan as an injectable wound dressing. *ACS Omega* 3, 4766–4775.
- Zhuang, C., Jiang, Y., Zhong, Y., *et al.*, 2018. Development and characterization of nano-bilayer films composed of polyvinyl alcohol, chitosan and alginate. *Food Control* 86, 191–199.

Polymer Composites for Organ Reconstruction

Haroon K Syed and Sajid Asghar, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Kai Bin Liew, University of Cyberjaya, Cyberjaya, Selangor, Malaysia

Ikram U Khan, Fizza A Razzaq, and Saba Rafique, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

© 2021 Elsevier Inc. All rights reserved.

Introduction of Composites

In terms of defining, composite is a combination of two or more components having different chemical as well as physical properties to acquire superior characteristics which cannot be acquired by any of the component on its own (Hashin, 1983). The word composite may sound new but it is as old as human history. The key point of the above-mentioned definition is creating something new by combining different materials. One of the best and oldest examples of a composite is adding straws to the mud to attain greater strength. Even nature has its own composites and some of the most prominent examples are leaves, wood and bone (Clyne and Hull, 2019).

At this point composites may seem like a blend or an amalgam of different materials but there is a striking difference between these two systems. In a blend or amalgam the individual components do not retain their identity however if we look at mud wall straws and mud have not lost their individual identity (Jones, 1998).

The usability of composite is not only limited to mud wall or wood instead the appliance of composite material has ached mankind into an era of airships, orthopedic devices, satellite systems, bulletproof vests, organ reconstruction and much more (Ngo, 2020).

Composition of a Composite

In general, a composite material comprises of three elements, which include a matrix, one or more reinforcement materials and an interface. Matrix and reinforcement are two major constituents of a composite material whereas the interface is the zone between them. The basic parts of a composite material system is presented in Fig. 1.

- (1) The material in bulk in a composite is called matrix. It is also known as continuous phase. The main role of a matrix is to act as a link and hold the reinforcement material in it. In addition, it must possess the capability to relocate the stress to the reinforcement material in it. Most frequently used matrix are divided into three group which include metals, ceramics and polymers (Jose and Joseph, 2012).
- (2) The material, which is dispersed in the matrix, is called reinforcement. It is also known as dispersed phase and its main function is to impart different properties to the system. Variety of reinforcement material has been studied throughout literature and each has the ability to impart different property to the composite. Some commonly used reinforcement material are fiber, particulate and laminates (Pastuszak and Muc, 2013).
- (3) Interface is not only responsible for relocating the stress from matrix phase to reinforcement phase but it can also influence the strength and overall properties of the composite system. At the interface, different types of bonding can be seen such as physical, chemical and mechanical. Stronger bonding imparts high strength to the composite but lower the toughness of the material and vice versa. Among all bonds chemical bond is strongest of all but it is avoided in the biomedical applications due to biocompatibility issues (Jesson and Watts, 2012).

Classification of Composites

Composites can be grouped on more than one basis however they are in general classified on the base of their constituents i.e. matrix and reinforcement. Different types of composites are mentioned in literature depending upon their constituents. On

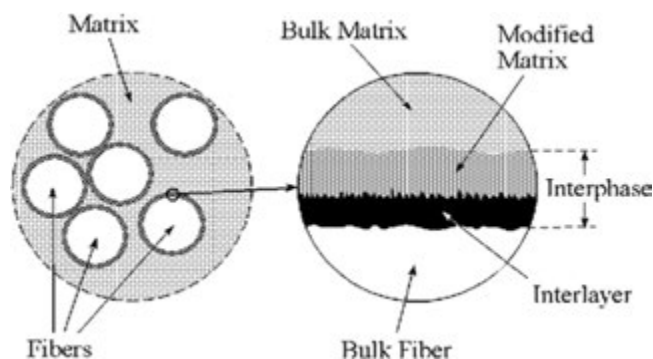


Fig. 1 Basic parts of a composite material system. Reproduced from Cech, V., Palesch, E., Lukes, J., 2013. The glass fiber–polymer matrix interface/interphase characterized by nanoscale imaging techniques, *Composites Science and Technology* 83, 22–26.

the base of the matrix, they are grouped into polymer matrix composite (PMC's), metal matrix composites (MMC's) and ceramic matrix composites (CMC's) and in case of reinforcement material they are divided into laminate composites, particulate composites and fibrous composites. However, in this article our focus will be polymeric matrix composites. (Balasubramanian, 2016).

Polymer Matrix Composites

A polymer matrix composite is generally defined as the material consisting of fibers either continuous or discontinuous, which are held together by the polymeric matrix. The only condition for a composite material to be considered polymeric in nature is to contain an organic polymer as its core or matrix. The addition of the term fiber in the definition comes from the extensive use of fiber to reinforce polymer. Such type of composites are typically known as fiber reinforced polymer composites. (Park and Seo, 2011) Like discussed above a reinforcing material can be particulate as well as laminate too. The only motive behind using fibers to reinforce polymers is their ability to efficiently carry load and improve the mechanical strength and stiffness of the composite system, which is lacked by the polymer matrix. Besides, in comparison to the other elements such as particles and laminates they own greater aspect ratio making them superior in strength. Some of key strengths of using fiber as reinforcing element are High modulus, High mechanical strength, Good corrosion and fatigue resistance, Lower cost, Easy fabrication methods, Good wetting properties and Multi-functional performance (Rajak *et al.*, 2019).

Polymers Used in PMCs

Fabrication of polymer composites involves varieties of polymer such as thermosetting polymers, thermostat polymers, elastomer and resorbable polymers. Furthermore, blends of these polymers can also be utilized however; selection of the polymer will be dependent upon the characteristics required of the composite system.

(1) Thermoplastic polymers:

These are high molecular weight polymers and their structure includes both linear as well as branched chain molecules, which are bonded by strong intra, and weak inter molecular bonds. In case of heating or applying pressure, these polymers cannot hold their shape and show softening or melting. As composites, they exhibit excellent stability and can be easily shaped into the desired contour exclusive of degradation. Examples include polyethylene, polypropylene, nylons, polystyrene, polyacetals, polysulfones (Wolf, 2000).

(2) Thermosetting polymers:

Reshaping phenomenon observed with the above-discussed type is unseen in these types of polymers. Their structure involves cross-linking and covalent bonds. As matrix, it shows curing phenomenon whereby polymer chain start to cross-link and gather the entire matrix in a 3D structure, which offers higher stability and temperature resistance. Epoxy, polyacrylates, polymethacrylates, polyesters, polyimides and ureas are some of the most prominent examples of this class (Rudyak *et al.*, 2019).

(3) Elastomers:

Polymers having high elasticity like rubber are known as elastomers. Their structure exhibit light cross-linking and weak bonding forces due to which they can be deformed easily. Besides, they also have a low modulus and glass transition temperature below room temperature. Natural rubber, silicone rubber, polysulfide rubber and thermoplastic elastomers are some of the commonly used examples. (Cardarelli, 2008).

(4) Resorbable polymers:

Resorbable polymers entail biodegradable chains, which can be degraded or dissolved in the body over time. Because of monomers along with species having small molecular weight are released which are engrossed by metabolic pathway. These types of composites materials are used majorly used in designing implants to bypass the need of surgical intervention to remove them. Some important resorbable polymers include poly lactide (PLA), poly glycolic acid (PGA), poly caprolactone (PCA) etc (Krishnamoorthy *et al.*, 2019).

Reinforcing Elements Used in PMCs

Among reinforcing materials, fiber is one of the most highlighted material for reinforcing polymer and is extensively employed in designing (Arpitha *et al.*, 2014). A typical fiber is produced as a continuous filament having diameter varying from 3 to 200 μm and can be assembled to manufacture yarn, town or mats. This fiber is known as long or continuous fiber and the composites reinforced by it are known as continuous fiber composites. However, the length of this fiber can also be decreased up to 0.02–100 mm. Such type of fibers are known as short or discontinuous fibers and they are involved in designing discontinuous fiber composites (Staab, 2015). Fibers can be oriented in different directions but they are mostly oriented in the direction of the stress to enhance the stress bearing capacity of the fibers. Even though both continuous and discontinuous fibers can be oriented but it is a little difficult to orient discontinuous fibers in comparison to long filaments (Campbell, 2010).

Types of fibers

(1) Natural fibers:

Fibers produced by plants, animals and geological processing are known as natural fibers. They are found abundantly in nature and are easily available but they display problems regarding processing which makes them costly and undesirable. In addition, their properties vary extremely. Some common examples of natural fibers include wood, wool, cotton, silk, jute and collagen (Taj *et al.*, 2007). Due to an increased trend of using natural materials for the sake of environment, researchers are more inclined towards using them.

(2) Synthetic fibers:

Synthetic fibers are manmade fibers that are synthesized chemically. In comparison to the natural fibers, they are more advantageous in terms of cost, properties as well as stability and are widely used in large number of application fields (Mahlitig and Kyosev, 2018). Use of these fibers in the fabrication of PMCs is extensive and can be found throughout the literature. However, some of the most pertinent examples are discussed below:

● Carbon fiber:

Carbon fibers (CF) consist of more than 90% of carbon atoms which are attached together to form a long chain with a diameter of 5–10 μm . These fibers are well known for their high strength, stiffness and lower weight making them an ideal candidate for use in prosthetic designing. In addition, carbon is inert in nature and it does not impede neotissue growth owing to this property. Instead, some studies also supported its positive role in enhancing the neotissue growth. Fabrication of carbon fibers involves using a precursor as raw material since pure carbon cannot be used for this purpose. The most widely used precursor is polyacetonitrile (PAN) (Pico and Steinmann, 2016; Kumar *et al.*, 2018).

● Glass fiber:

These fibers are fabricated by melting silica followed by extrusion and attenuation to form filaments, which are further thinned by drawing. In terms of strength, they are inferior to carbon fiber. However, they exhibit little brittleness and are less costly as compared to CF. Also due to their transparency, resistant nature and biocompatibility they are widely used in dental composite fabrication. Apart from that they also used as biomaterials for orthopedic implants and their components (Mahlitig and Kyosev, 2018; Syed *et al.*, 2019).

● Polymeric fiber:

Due to their versatile nature and greater resemblance with extra cellular matrix, fibers are majorly employed in tissue engineering. Basic method to manufacture polymer fibers is spinning polymer solution followed by stretching. Spinning turns the solution to a fibrous form whereas stretching orients the polymer chains enhancing the modulus as well as strength of the fiber (Bhat and Kandagor, 2014). Most frequently used polymer fibers include aramid fibers (Kevlar T^M), Polyethylene fibers and Poly ethylene glycol terephthalate fibers (Dacron T^M). Resorbable Fiber such as PLA, PLGA, PGA consist of resorbable polymers and are used where dissolution of the composite is required which is necessitated to decrease the mechanical properties over time or to address the issue of removing the implant with surgery (Ratner *et al.*, 2004).

Properties of PMCs

Designing a PMCs involve considering a large number of variables which can shape the overall properties of the system. Each constituent has its own properties and it will affect the composite system depending upon these set of properties. Apart from these, some other variables are important, which include shape and orientation of dispersed phase as well as interfacial adhesion. (Atay, 2016) In order to obtain an optimized composite material each of these factors should be controlled vigilantly.

(1) Shape and orientation of dispersed phase:

All the reinforcement materials have different shapes and orientations and each can influence composite system in its own unique way. Such as fibers which can be long or short and are oriented in a direction to which stress is applied to impart more strength to the system. Similarly, laminates are in the form of sheet having multiple layers, which are oriented to provide increased strength from two directions. Subsequently particles can be sphere, cube, regular or irregular in shape with no favored direction (Clyne and Hull, 2019).

(2) Interfacial Adhesion:

The performance of a composite system is heavily dependent on the ability of matrix and reinforcement materials to adhere to each other. The adhesion can be physical, mechanical or even chemical. Greater the adhesion superior will be the properties in terms of strength and stability (Sottos and McCullough, 1994).

Manufacturing Methods of Polymer Matrix Composites

A large number of methods are involved in manufacturing polymer matrix composites such as pultrusion, hand layup, Spray layup, filament winding, resin transfer molding and injection molding. The key strength of all these methods is easy and less costly fabrication. However, they can be divided in two types based on molds. The mold can be open as well as closed. Subsequently the selection depends on the type of end product required as well as desired application. When the polymeric matrix is in contact with the atmosphere it is termed as open molding method also known as contact molding whereas the latter involve no such contact as

the matrix is enclosed in the mold (Kesarwani *et al.*, 2015). In terms of price, open molded methods are less costly in comparison to closed molded one. In addition, the final products obtained by both are poles apart. The former ones are mostly used when there is a need to produce bulky sized parts but they are also important in producing small parts when cost is an issue. Closed molding is used when the surface of material is supposed to be smooth from both sides as well as to produce accurate parts in bulk (Zulkepli *et al.*, 2019).

Open molded methods

(1) Hand lay up:

It is a very simple and popular technique, which involves layering matrix and reinforcing materials in an open mold by hand. The reinforcing fiber can be continuous, chopped or even woven. One of the biggest advantages offered by this method is higher quality but it is limited by very low production rate. In order to fabricate a high quality polymer composite, an antiadhesive agent followed by another coating also called gel coating to ensure easy release and enhance the quality of the surface respectively usually covers the mold. The reinforcing material is then arranged and covered by resin, which should be evenly distributed. Each layer is stuck to the previous one and if needed rolled to avoid any air pockets. These impregnated layers are then cured and removed from the mold (Cripps *et al.*, 2000; Raji *et al.*, 2019).

(2) Spray up:

This technique is similar to the former technique except it is less rigorous and time consuming than the previous one. In addition, the properties of the composite material such as thickness and the quality lies on the expertise of the machinist. The basic mechanism involves spraying the matrix and reinforcing fibers with the help of a spray gun or jet. Both liquid polymer and the reinforcing material are sprayed concurrently into mold at a preset ratio followed by rolling to remove any air pocket and curing. Furthermore, the fibers are chopped before spraying, as it is not suitable for continuous fibers. This method offer uniform coating but the mechanical properties are lower as compared to hand layup method due to short length of fibers and their random orientation (Cripps *et al.*, 2000; Raji *et al.*, 2019).

(3) Filament winding:

This method involves winding of long filament bundles around the mandrel that is continuously in a rotating motion followed by curing in the oven to solidify the material. Winding can be helical, in loop or in polar style. Although this method is majorly used for thermoset matrixes but in case of thermoplastic material, the mandrel is heated before winding. The first step involves impregnation of the reinforcing fibers bundles with the resin, which is usually done in resin bath. After the impregnation comes winding which can be performed at different angles and in different patterns. Because of winding, a hollow tubular structure is obtained which is first cured and then subsequently removed from the mandrel (Mack and Schledjewski, 2012; Quanjin *et al.*, 2018).

Closed molded methods

(1) Pultrusion:

As indicated by the name this technique is a combination of two things i.e., pulling and extrusion. Fiber from the creel is pulled in to the guided plate to make a bundle of the fibers, which is further guided in to the resin bath where impregnation of the reinforcing material takes place. To shape the composite, the impregnated fibers pass through a device known as performer before entering the die. Performer remove excess matrix from the fibers. In the die, curing take place and the final product is extruded out from the die in the form of rods and beams. This method is best for making composite material rods and beams of high strength because of high fiber fraction. Also the reinforcement provided by this method is continuous (Wilson, 1998; Joshi, 2012).

(2) Resin transfer molding:

This method includes using a closed mold, which provides a better quality finishing product and it usually engage thermosetting resins and continuous fibers. The process entails using three things, which include a closed mold, a transfer pot and a plunger. The first step involves the placement of precut reinforcement material inside the closed mold followed by heating of matrix in the transfer pot. If any additives required they are usually added at this stage along with matrix. After that plunger, forcing it in to the mold presses the resin and additives. The mold is equipped with heater to allow the thermosetting polymer to cure and form crosslinked structure. Ejection takes place after the curing of the matrix because a thermoset matrix retains its shape however in terms thermoplastic resins cooling is required. In comparison to open molding techniques this process is faster and it can produce complex shapes but it necessitates skillfully intended molds (Laurenzi and Marchetti, 2012; Sozer *et al.*, 2012).

(3) Injection molding:

This method is majorly used for processing of discontinuous fibers. The method involves feeding blend of polymer and short fibers in pellets form to the hopper, which conveys the pellet to heated barrel having reciprocating screws, which along with rotary motion can also move forward and backward. The forward movement is intended to shift the fed from hopper to mold followed by the backward shift. Inside heated barrel, mixing takes place followed by forcing it through a small cavity to the mold. The configuration given by mold hardens and solidify upon cooling. This method is advantageous in many ways, which include fastest rate, complex shapes, high rate of production, higher volume and tolerability, but it is limited in terms of fiber length, as well as their orientation across the matrix material. As far as matrix is concerned thermoplastic materials are

Table 1 Examples of different polymer composites employed in reconstructing different organs

Application		Polymer composites (reinforcing element/matrix)	References
Bone reconstruction	Bone plates	Carbon fiber/Polyetheretherketone (PEEK)	(Fujihara <i>et al.</i> , 2003)
		Carbon fiber/Epoxy	(Veerabagu <i>et al.</i> , 2003)
		Polyglycolic acid (PGA)/polyglycolic acid (PGA)	(Tormala, 1992)
	Intramedullary nails or rods	Carbon fiber/Polyether ether ketone (PEEK) rod	(Lin <i>et al.</i> , 1997; Zimel <i>et al.</i> , 2015)
Joint reconstruction	Hip replacement	CF/Ultra high molecular weight polyethylene (UHMWPE)	(Rushton and Rae, 1984)
		Acetubular cup	
		Carbon fiber/Carbon stem	(Christel <i>et al.</i> , 1987)
		CF/Epoxy stem	(Chang <i>et al.</i> , 1990)
	Knee replacement	CF/Polyether ether ketone (PEEK) stem	(Wintermantel <i>et al.</i> , 1994)
		CF/Ultra high molecular weight polyethylene (UHMWPE)	(Wright <i>et al.</i> , 1981)
		tibial component	
	Bone cement	UHMWPE/Poly methyl methacrylate (PMMA)	(Yang <i>et al.</i> , 1997)
PMMA/PMMA		(Gilbert <i>et al.</i> , 1995)	
CF/PMMA		(Pilliar <i>et al.</i> , 1976)	
Dental reconstruction	Dental post	GF/BIS-GMA and CF/epoxy posts	(Ferrari <i>et al.</i> , 2000; Soares <i>et al.</i> , 2008; Lamichhane <i>et al.</i> , 2014)

preferred but thermosetting polymers can also be used but they require curing which can take place during heating inside the barrel (Kamal and Isayev, 2012; Liu, 2012).

Applications of Polymer Composites

Applications of polymer composites can be found in various fields of life but in this article, we will only focus on organ reconstruction. Reconstructing an organ is better approach to manage damaged organs as compared to transplant but reconstructing a whole organ is not an easy task (Stoltz *et al.*, 2017). Different researches are being conducted to achieve this goal and because of these efforts, different bones, teeth, joints and even tissues can be reconstructed successfully. An overview of these published reports are presented in Table 1, which briefly summarizes some examples of polymer composite materials employed in reconstructing different organs.

Bone reconstruction

Human body consist of approximately 206 bones which combinedly frames the skeletal system and give support to the body however these bones can modify or even break under high stress conditions (Matassi *et al.*, 2011). Fixing a bone can be done in two ways. First, one is external fixing with the help of casts or splints and second one is internal fixation, which is a surgical procedure and is done in serious conditions where bone needs to be supported by using orthopedic implants until the healing has occurred. After the complete healing of the bone these implants are removed from the body. These implants are commonly known as bone plates and intramedullary nails (Saad *et al.*, 2018). In the beginning, these supporting systems were made of metal and titanium however, the modulus of these materials was higher in comparison to bone, which caused the bone to lose its density due to absence of typical stress and fracture again once these implants are removed. This phenomenon is also known as shear shielding. To avoid this phenomena a material having modulus closer to bone as well as sufficient mechanical strength was needed making polymers a suitable option (Ritchie, 1988; Saad *et al.*, 2018).

(1) Bone plates:

Using polymeric composites different types of bone plates can be fabricated. In the beginning, non resorbable composite plates were made using epoxy polymer (Bradley *et al.*, 1980; McKenna *et al.*, 1980) as bulk phase (CF/EPOXY, GF/EPOXY) (Fig. 2(a)), but due to their toxic effect on the body, they were replaced with thermoplastic matrixes like carbon fiber reinforced PMMA, CF/polypropylene, CF/PE, CF/polysulfone, CF/nylon and CF reinforced PEEK (Fig. 2(b)) due to their toxicity free application and ability to bent by heat (Krebs *et al.*, 1997; Fujiyama *et al.*, 2001; Jockisch *et al.*, 1992). Although these composite plates were a success but healing process can be made more efficient by making the plate to lose its rigidity with time which was accomplished by using polymers which are resorbable in nature. However, plates manufactured by using these polymers lack the mechanical strength required to hold the bone, which was enhanced by reinforcing with fiber. If the reinforcing material used is resorbable in nature, then these plates will be known as resorbable composite plates and if it is non resorbable such as carbon fibers and polyamide fibers, then it will be known as partial resorbable composite plates (Ahmed *et al.*, 2011; Mehboob and Chang, 2014).

(2) Intramedullary nails:

These are rod like structures, which are placed in the intramedullary cavity of the femoral-neck bone and inter trochanteric bone. In comparison to bone plates they are used to fix long bone fractures owing to their better mechanical support which is attributed to their central placement on the bone (Hench, 2005). One of the most successfully used material for the fabrication of the

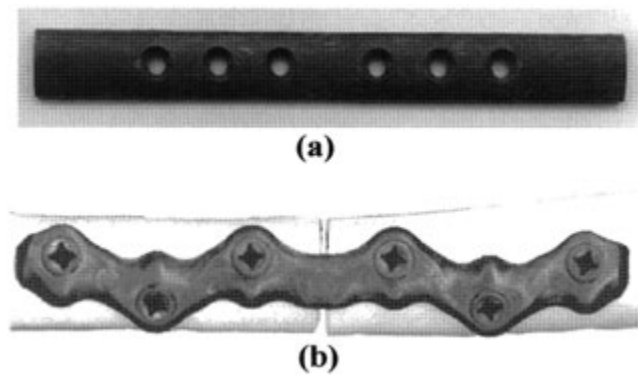


Fig. 2 (a) A typical composite bone plate made of CF/epoxy material (b) composite bone plate made of CF/PEEK. Reproduced from Ramakrishna, S., Huang, Z.M., Kumar, G.V., Batchelor, A.W., Mayer J., 2004. *An Introduction to Biocomposites*. London: Imperial College Press, 223.



Fig. 3 Intramedullary nails made up of CF/PEEK composite system. Reproduced from Hak, D.J., Mauffrey, C., Seligson, D., Lindeque, B., 2014. Use of carbon-fiber-reinforced composite implants in orthopedic surgery. *Orthopedics* 37 (12), 825–830.

intramedullary nails is CF /PEEK composite (consisting of polyether ether ketone polymer which is reinforced with glass fiber) is shown in **Fig. 3** which exhibited good mechanical properties along with biocompatibility (Vles *et al.*, 2019).

Joint replacement

Joints provide mobility to the body and with regard to design; mostly joints are located between two bones and are shielded and lubricated by a layer of cartilage and synovial fluid respectively. Like bones, joints can also be injured permanently or deteriorated with time due to any disease such as arthritis, which is one of the leading causes of affecting joints. Joint implant is a permanent placement of an artificial joint in the body in order to replace damaged joints. Most common joint implants are knee and hip replacement.

(1) Hip replacement:

The design of the hip replacement implant basically contains a femoral stem and an acetabular cup in which the head of the stem is fixed (Arun *et al.*, 2014) and the material used for its manufacturing include cobalt and chromium alloy, alumina and zirconia, titanium alloy and stainless steel (Pramanik *et al.*, 2005). A hip replacement implant is shown in **Fig. 4**. To avoid metal particles, John Charnley utilized a polymer named Polytetrafluoroethane (PTFE) in 1956 for making of cups owing to its stability and inertness, which under stress showed high wear damage and even tissue reaction. It was later replaced by ultra-high molecular weight polyethylene (UHMWPE) with metallic backing, which also proved to be failure in the long run. It showed creep phenomena as well as erosion which was attributed to metal backing (Merola and Affatato, 2019). To avoid this failure, polymer composites of UHMWPE were used by reinforcing with carbon fibers (CF). They not only bypassed creep phenomena but also provided superior bone bonding and longer life (implant). However these effects were contradictory as some studies negated these benefits (Rushton and Rae, 1984). Due to the concerns with CF polymeric (UHMWPE) fibers were used to reinforce UHMWPE polymer (Deng and Shalaby, 1997). Similarly polyether ether ketone has also been successfully utilized in manufacturing of acetabular cup (Merola and Affatato, 2019). As far as stems are concerned, one of the biggest issue associated with metallic stems is the difference in the stiffness of the metal and bone, which cause the bone to resorb and ultimately cause the implant to loosen up. This issue could be reduced by using alloys such as co-cr alloy and titanium alloy but In order to resolve it such material is required which is comparable in stiffness to bone as well as strong too. To achieve this goal different types of composite material were used by researchers owing to their unique properties and some major examples include CF/EPOXY and CF/PEEK. Although these polymeric composites are more advanced as compared to conventionally used material and offer more advantages in comparison but they are still not in practice (Karihaloo *et al.*, 2003).

(2) Knee replacement:

Knee is a very complicated joint and replacing it involves replacing femur and tibia bone. Building material for femur bone component involve co-cr and Ti alloys whereas for tibial bone ultra-high molecular weight polyethylene and metals are used (Carr and Goswami, 2009). An implant of knee replacement is presented in **Fig. 5**. UHMW polyethylene was reported to

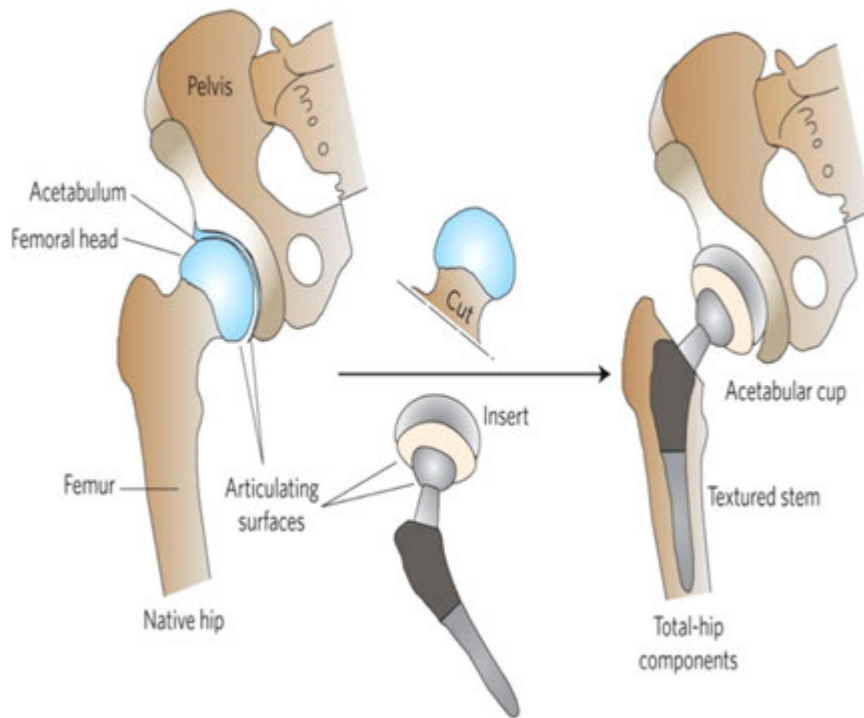


Fig. 4 Hip replacement implant. Reproduced from Hickok, N.J., 2017. Joint implants: An elution solution, *Nature Biomedical Engineering* 1 (6), 0087.

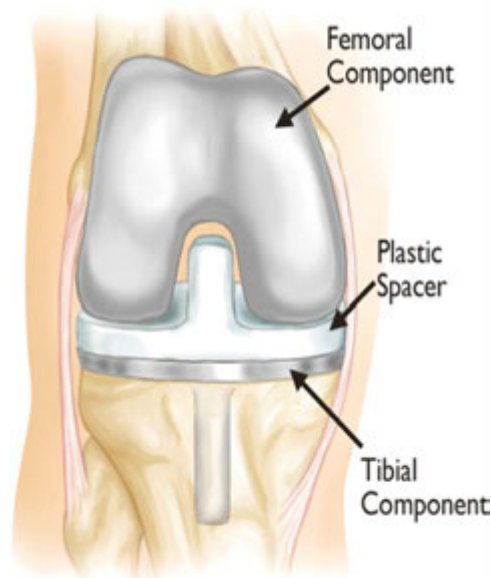


Fig. 5 Knee replacement implant. Reproduced with permission from OrthoInfo. © American Academy of Orthopaedic Surgeons. <http://orthoinfo.aaos.org>.

undergo creep phenomena because of which implant started to sinking. To avoid this phenomenon, it was reinforced with carbon fiber. The reinforcement demonstrated good results in regard to strength and sinking however its effect on wear damage were contradictory (Saad *et al.*, 2018).

(3) Bone cement:

Artificial joints are fixed to the bone by using a material known as bone cement. Acrylic bone cement is one of the most extensively used bone cement. It is self- polymerizing in nature and basically consist of two components i.e. PMMA in powder form and MMA monomer in liquid state (Kaivosoja *et al.*, 2013).The drawback of this cement is that it can cause bone necrosis locally. Due to its polymerizability temperature of the local tissue gets raised and monomers are released in the

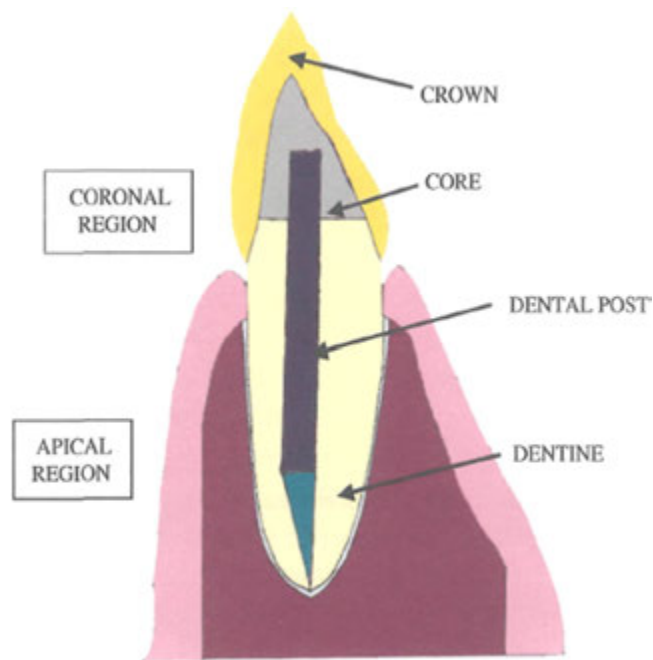


Fig. 6 A dental post restored tooth. Reproduced from Panitiwat, P., Salimee, P., 2017. Effect of different composite core materials on fracture resistance of endodontically treated teeth restored with FRC posts. *Journal of Applied Oral Science* 25 (2), 203–210.

blood. Due to increased temperature necrosis may occur (Kaivosoja *et al.*, 2013) but it can be avoided by reinforcing the bone cement with variety of fibers such as inorganic fibers (Kevlar carbon stainless steel, Ti alloys) and polymeric fibers (UHMWPE, PMMA) which along with subsiding necrosis also enhanced the strength. Despite being more effective these fiber reinforced bone cement are not found in practice due to following reasons (Shalaby and Salz, 2006).

1. Viscosity of bone cement increase by reinforcing.
2. Achieving uniform distribution of fibers throughout bone cement is difficult.

Dental reconstruction

The scope of polymer composites in dental field is higher and can range from restoring a tooth to replacing it. Variety of PMCs are used in dental treatments such as dental restoration, veneering and dental post. Each treatment details have been mentioned below.

(1) Dental restorative materials:

Dental composite resin consisting of polymer matrix and a filler is used for the purpose of filling dental cavities as well as veneering. Polymers that can be used as matrix are Bis Phenol A, glycidyl methacrylate and urethane dimethacrylate. However, the former one is used in most cases. In terms of fillers, glass fiber is extensively used owing to its ability to reduce wear damage and transparency. Besides that it also helps in reducing the shrinking observed due to polymerization of the resin composites along with the reduction in the thermal coefficient expansion which can cause mismatch between the modulus of the resin and teeth (Zhou *et al.*, 2019).

(2) Dental post:

Dental post is known as pins, which are used in the case where teeth cannot maintain filling due to the absence of the adequate structure. conventionally they are manufactured using metals and alloys (nickel chromium, aluminum, platinum, titanium and stainless steel) which resulted in corrosion fracture, less retention due to higher modulus of dental post as compared to dentine (Machado *et al.*, 2017). Keeping in view of all the requirements newer dental post were fabricated using polymer composites, which not only decreased the fracture rate but also reduced the stress at dentine, which is root cause of post loosening. The composite material involved in manufacturing dental composites are polyester matrix reinforced with short glass fiber and epoxy matrix with unidirectional carbon fiber. Fig. 6 presents a dental post of a restored tooth.

References

- Ahmed, I., Jones, I.A., Parsons, A.J., *et al.*, 2011. Composites for bone repair: Phosphate glass fibre reinforced PLA with varying fibre architecture. *Journal of Materials Science: Materials in Medicine* 22 (8), 1825–1834.
- Arpitha, G.R., Sanjay, M.R., Yogesha, B., 2014. Review on comparative evaluation of fiber reinforced polymer matrix composites. *Advanced Engineering and Applied Sciences: An International Journal* 4, 44–47.

- Arun, S., Rama Sreekanth, P.S., Kanagaraj, S., 2014. Polymer composites for cemented total hip replacements. In: Davim, J.P. (Ed.), *Biomedical Composites: Materials, Manufacturing, and Engineering*. Berlin/Boston: Walter De Gruyter, pp. 53–63.
- Atay, H.Y., 2016. Polymer composites; Properties, performance and applications. In: Méndez-Vilas, A., Solano, A. (Eds.), *Polymer Science: Research Advances, Practical Applications and Educational Aspects*. Formatex Research Center, pp. 420–428.
- Balasubramanian, M., 2016. Introduction to Composite Materials. Fibrous and Textile Materials for Composite Applications. Springer. pp. 1–38.
- Bhat, G., Kandagor, V., 2014. Synthetic polymer fibers and their processing requirements. In: Zhang, D. (Ed.), *Advances in Filament Yarn Spinning of Textiles and Polymers*. Elsevier, pp. 3–30.
- Bradley, J.S., Hastings, G.W., Johnson-Nurse, C., 1980. Carbon fibre reinforced epoxy as a high strength, low modulus material for internal fixation plates. *Biomaterials* 1 (1), 38–40.
- Campbell, F.C., 2010. *Structural Composite Materials*. Materials Park, OH: ASM international.
- Cardarelli, F., 2008. Polymers and elastomers. In: *Materials Handbook: A Concise Desktop Reference*. London: Springer, pp. 691–750.
- Carr, B.C., Goswami, T., 2009. Knee implants—Review of models and biomechanics. *Materials & Design* 30 (2), 398–413.
- Chang, F.K., Perez, J.L., Davidson, J.A., 1990. Stiffness and strength tailoring of a hip prosthesis made of advanced composite materials. *Journal of Biomedical Materials Research* 24 (7), 873–899.
- Christel, P., Meunier, A., Leclercq, S., Bouquet, P., Buttazoni, B., 1987. Development of a carbon-carbon hip prosthesis. *Journal of Biomedical Materials Research* 21 (A2 Suppl), 191–218.
- Clyne, T., Hull, D., 2019. Front matter. In: *An Introduction to Composite Materials*. Cambridge: Cambridge University Press, pp. 1–6.
- Cripps, D., Searle, T.J., Summerscales, J., 2000. Open mold techniques for thermoset composites. In: Kelly, A., Zweben, C. (Eds.), *Comprehensive Composite Materials*, vol. 2. Elsevier, pp. 737–761.
- Deng, M., Shalaby, S.W., 1997. Properties of self-reinforced ultra-high-molecular-weight polyethylene composites. *Biomaterials* 18 (9), 645–655.
- Ferrari, M., Vichi, A., García-Godoy, F., 2000. Clinical evaluation of fiber-reinforced epoxy resin posts and cast post and cores. *American Journal of Dentistry* 13 (Spec No), 15B–18B.
- Fujihara, K., Huang, Z.M., Ramakrishna, S., Satknanantham, K., Hamada, H., 2001. Development of braided carbon/PEEK composite bone plates. *Advanced Composites Letters* 10 (1), 13–20.
- Fujihara, K., Huang, Z.M., Ramakrishna, S., Satknanantham, K., Hamada, H., 2003. Performance study of braided carbon/PEEK composite compression bone plates. *Biomaterials* 24 (15), 2661–2667.
- Gilbert, J.L., Diane, S.N., Eugene, P.L., 1995. Self-reinforced composite poly (methyl methacrylate): Static and fatigue properties. *Biomaterials* 16 (14), 1043–1055.
- Hashin, Z., 1983. Analysis of Composite Materials—A survey. *Journal of Applied Mechanics* 50 (3), 481–505.
- Hench, L.L., 2005. Repair of skeletal tissues. In *Biomedical, Artificial Organs and Tissue Engineering*. Elsevier. pp. 119–128.
- Jesson, D.A., Watts, J.F., 2012. The interface and interphase in polymer matrix composites: Effect on mechanical properties and methods for identification. *Polymer Reviews* 52 (3), 321–354.
- Jockisch, K., Brown, S.A., Bauer, T.W., Merritt, K., 1992. Biological response to chopped-carbon-fiber-reinforced peek. *Journal of Biomedical Materials Research* 26 (2), 133–146.
- Jones, R.M., 1998. *Mechanics of Composite Materials*. CRC press. Taylor & Francis.
- Jose, J.P., Joseph, K., 2012. Advances in polymer composites: Macro-and microcomposites – State of the art, new challenges, and opportunities. In: Thomas, S., Kuruville, J., Malhotra, S.K., Goda, K., Sreekala, M.S. (Eds.), *Polymer Composites*. Wiley, pp. 1–16.
- Joshi, S., 2012. Chapter – 12 The pultrusion process for polymer matrix composites. In: Advani, S.G., Hsiao, K.-T. (Eds.), *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. Elsevier, pp. 381–413.
- Kaivosoja, E., Tiainen, V.M., Takakubo, Y., *et al.*, 2013. Materials used for hip and knee implants. In: Afatato, S. (Ed.), *Wear of Orthopaedic Implants and Artificial Joints*. Elsevier, pp. 178–218.
- Kamal, M.R., Isayev, A.I., 2012. *Injection Molding: Technology and Fundamentals*. Carl Hanser Verlag GmbH Co KG.
- Karihaloo, B.L., *et al.*, 2003. *Comprehensive Structural Integrity: 10 Volume Set*. Elsevier.
- Kesarwani, P., Shahnaz, J., Kirti, K., 2015. Composites: Classification and its manufacturing process. *International Journal of Applied Research* 1 (9), 352–358.
- Krebs, J., Friedrich, K., Heuwinkel, R., Rieger, P., Kosack, P., 1997. Fibre-reinforced thermoplastic composite osteosynthesis implants with variable mechanical properties for better treatment of bone fractures. *Proceedings of ICCM–11*. 509–517.
- Krishnamoorthy, G., Gopal, P., Danaboyina, R., 2019. Resorbable polymer matrices: Chitosan-substituted collagen-based biomaterials. In: Grumezescu, V., Grumezescu, A.M. (Eds.), *Materials for Biomedical Engineering*. Elsevier, pp. 245–278.
- Kumar, N., Gangwar, A.K., Sangeeta, K.D., 2018. Chapter – 6 Carbon fibers in biomedical applications. In: Khanna, R., Cayumil, R. (Eds.), *Recent Developments in the Field of Carbon Fibers*. Intechopen, pp. 83–102.
- Lamichhane, A., Chun, X., Fu-qiang, Z., 2014. Dental fiber-post resin base material: A review. *The Journal of Advanced Prosthodontics* 6 (1), 60–65.
- Laurenzi, S., Marchetti, M., 2012. Advanced composite materials by resin transfer molding for aerospace applications. In: Hu, N. (Ed.), *Composites and Their Properties*. IntechOpen, pp. 197–226.
- Lin, T., Corvelli, A.A., Frondoza, C.G., Roberts, J.C., Hungerford, D.S., 1997. Glass peek composite promotes proliferation and osteocalcin production of human osteoblastic cells. *Journal of Biomedical Materials Research* 36 (2), 137–144.
- Liu, S.J., 2012. Injection molding in polymer matrix composites. In: Advani, S.G., Hsiao, K.-T. (Eds.), *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. Elsevier, pp. 15–46.
- Machado, J., Almeida, P., Fernandes, S., Marques, A., Vaz, M., 2017. Currently used systems of dental posts for endodontic treatment. *Procedia Structural Integrity* 5, 27–33.
- Mack, J., Schledjewski, R., 2012. Filament winding process in thermoplastics. In: Advani, S.G., Hsiao, K.-T. (Eds.), *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. Elsevier, pp. 182–208.
- Mahlitig, B., Kyosev, Y., 2018. *Inorganic and Composite Fibers: Production, Properties, and Applications*. Elsevier. pp. 1–29.
- Matassi, F., Nistri, L., Chicon Paez, D., Innocenti, M., 2011. New biomaterials for bone regeneration. *Clinical Cases in Mineral and Bone Metabolism* 8 (1), 21.
- McKenna, G., Bradley, G.W., Dunn, H.K., Statton, W.O., 1980. Mechanical properties of some fibre reinforced polymer composites after implantation as fracture fixation plates. *Biomaterials* 1 (4), 189–192.
- Mehboob, H., Chang, S.H., 2014. Application of composites to orthopedic prostheses for effective bone healing: A review. In: Ferreira, A.J.M. (Ed.), *Composite Structures* 118. Elsevier, pp. 328–341.
- Merola, M., Afatato, S., 2019. Materials for hip prostheses: A review of wear and loading considerations. *Materials* 12. 495.
- Ngo, T.D., 2020. Introduction to composite materials. In: *Fiber Composites*. IntechOpen.
- Park, S.J., Seo, M.K., 2011. Types of composites. *Interface Science and Technology* 18, 501–629.
- Pastuszak, P.D., Muc, A., 2013. Application of composite materials in modern constructions. *Key Engineering Materials*. 119–129.
- Pico, D., Steinmann, W., 2016. Synthetic fibres for composite applications. In: Rana, S., Figueiro, R. (Eds.), *Fibrous and Textile Materials for Composite Applications*. Springer, pp. 135–170.
- Pilliar, R., Blackwell, R., Macnab, I., Cameron, H.C., 1976. Carbon fiber-reinforced bone cement in orthopedic surgery. *Journal of Biomedical Materials Research* 10 (6), 893–906.

- Pramanik, S., Agarwal, A.K., Rai, K.N., 2005. Chronology of total hip joint replacement and materials development. *Trends in Biomaterials & Artificial Organs* 19 (1), 15–26.
- Quanjin, M., Rejab, M.R.M., Jiang, K., Idris, M.S., Harith, M.N., 2018. Filament winding technique, experiment and simulation analysis on tubular structure. *IOP Conference Series: Materials Science and Engineering* 342.
- Rajak, D.K., Pagar, D.D., Menezes, P.L., Linul, E., 2019. Fiber-reinforced polymer composites: Manufacturing, properties, and applications. *Polymers* 11, 1667.
- Raji, M., *et al.*, 2019. Prediction of the cyclic durability of woven-hybrid composites. In *Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*. Elsevier. pp. 27–62.
- Ratner, B.D., *et al.*, 2004. *Biomaterials Science: An Introduction to Materials in Medicine*. Elsevier.
- Ritchie, R., 1988. Mechanisms of fatigue crack propagation in metals, ceramics and composites: Role of crack tip shielding. *Materials Science and Engineering: A* 103 (1), 15–28.
- Rudiyak, V.Y., Efimova, E.A., Guseva, D.V., Chertovich, A.V., 2019. Thermoset polymer matrix structure and properties: Coarse-grained simulations. *Polymers* 11, 36.
- Rushton, N., Rae, T., 1984. The intra-articular response to particulate carbon fibre reinforced high density polyethylene and its constituents: An experimental study in mice. *Biomaterials* 5 (6), 352–356.
- Saad, M., Akhtar, S., Srivastava, S., 2018. Composite polymer in orthopedic implants: A review. *Materials Today: Proceedings* 5 (9), 20224–20231.
- Shalaby, S.W., Salz, U., 2006. *Polymers for Dental and Orthopedic Applications*. CRC Press.
- Soares, C.J., Santana, F.R., Pereira, J.C., Araujo, T.S., Menezes, M.S., 2008. Influence of airborne-particle abrasion on mechanical properties and bond strength of carbon/epoxy and glass/bis-GMA fiber-reinforced resin posts. *The Journal of Prosthetic Dentistry* 99 (6), 444–454.
- Sottos, N.R., McCullough, R., 1994. *Interphase in Polymer-matrix Composites*. vol. 2. ASME.
- Sozer, E., *et al.*, 2012. Chapter – 9 Resin transfer molding (RTM) in polymer matrix composites. In: Advani, S.G., Hsiao, K.-T. (Eds.), *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. Elsevier, pp. 245–309.
- Staab, G.H., 2015. *Laminar Composites*. Butterworth-Heinemann.
- Stoltz, J.F., Zhang, L., Ye, J.S., De Isla, N., 2017. Organ reconstruction: Dream or reality for the future. *Bio-Medical Materials and Engineering* 28 (s1), S121–S127.
- Syed, M.R., *et al.*, 2019. Bioactive glass and glass fiber composite: Biomedical/dental applications. In *Biomedical, Therapeutic and Clinical Applications of Bioactive Glasses*. Elsevier. pp. 467–495.
- Taj, S., Munawar, A., Khan, S.U., 2007. Natural fiber-reinforced polymer composites. *Proceedings-Pakistan Academy of Sciences* 44 (2), 129.
- Tormala, P., 1992. Biodegradable self-reinforced composite materials; manufacturing structure and mechanical properties. *Clinical Materials* 10 (1–2), 29–34.
- Veerabagu, S., Fujihara, K., Dasari, G.R., Ramakrishna, S., 2003. Strain distribution analysis of braided composite bone plates. *Composites Science and Technology* 63 (3–4), 427–435.
- Vies, G.F., Maximillian, H.B., Mark, A.R., James, Y., 2019. Carbon-fiber-reinforced PEEK intramedullary nails defining the niche. *Case Reports in Orthopedics*. 1–6.
- Wilson, B.A., 1998. Pultrusion. In: Peters, S.T. (Ed.), *Handbook of Composites*. Springer, pp. 488–524.
- Wintermantel, E., *et al.*, 1994. CAD, CAE and CAM for a new anisotropic carbon fiber reinforced hip endoprosthesis stem, technology, test procedures and qualifying preclinical results. *Biomedical Engineering: Applications, Basis and Communications* 6, 18–21.
- Wolf, C.J., 2000. Composite materials, thermoplastic polymer-matrix. In *Kirk-Othmer Encyclopedia of Chemical Technology*. Wiley.
- Wright, T., Fukubayashi, T., Burstein, A.H., 1981. The effect of carbon fiber reinforcement on contact area, contact pressure, and time-dependent deformation in polyethylene tibial components. *Journal of Biomedical Materials Research* 15 (5), 719–730.
- Yang, J.M., Huang, P.Y., Yang, M.C., Lo, S.K., 1997. Effect of MMA-g-UHMWPE grafted fiber on mechanical properties of acrylic bone cement. *Journal of Biomedical Materials Research* 38 (4), 361–369.
- Zhou, X., *et al.*, 2019. Development and status of resin composite as dental restorative materials. *Journal of Applied Polymer Science* 136 (44), 48180.
- Zimel, M.N., Hwang, S., Elyn, R.R., John, H.H., 2015. Carbon fiber intramedullary nails reduce artifact in postoperative advanced imaging. *Skeletal Radiology* 44 (9), 1317–1325.
- Zulkepli, I., Mokhtar, H., Aminanda, Y., Shaik Dawood, M.S.I., Rehan, M.S.M., 2019. Review of manufacturing process for good quality of composite assessment. *IOP Conference Series: Materials Science and Engineering* 488.

Overview of Additive Manufacturing Biopolymer Composites

Bankole I Oladapo and S Abolfazl Zahedi, De Montfort University, Leicester, United Kingdom

Vincent A Balogun, Edo University Iyamho, Iyamho, Edo State, Nigeria

Sikiru O Ismail, University of Hertfordshire, Hatfield, United Kingdom

Yarjan A Samad, University of Cambridge, Cambridge, United Kingdom

© 2021 Elsevier Inc. All rights reserved.

Introduction

Additive manufacturing (AM) initially used a polymer substrate for the production of parts. However, as the research continues, metals and ceramic composites became substitutes. These materials are used to support the progression, not to give the anticipated product in AM. For example, various polymers are adapted for different roles as adhesion promoters, plasticisers, and surfactants in fused deposition modelling (FDM) (Tofail *et al.*, 2018; Oladapo *et al.*, 2020d,e; Oluwole *et al.*, 2020; Zahedi *et al.*, 2013, 2019). Layered production, commonly referred to as AM, is a sophisticated manufacturing technique that adds layered material in subset to create three-dimensional (3D) products, using computer-aided design (CAD) models. The most significant benefit of AM is that it eliminates complex manufacturing processes when it comes to geometric complexities and elements that cannot be created with subtractive manufacturing processes. In many studies, various AM processes' operating principles are preserved and mostly used categories, depending on the starting material's condition. Table 1 shows the material working principle for AM presenting process types, layer technology, and conventional materials (Bikas *et al.*, 2016; Umme *et al.*, 2016). The complicated concepts and working principles of electron beam melting (EBM), selective laser melting (SLM), fused deposition modelling (FDM), selective laser sintering (SLS), stereolithography (SLA) and multi-jet modelling (MJM) are subsequently discussed.

The application of modern technology in AM requires materials containing a mixture of traditional ceramics, ceramics, or unusual properties that are not found in polymers. The blended materials synthesise new materials, using two or more materials with desired properties to produce the final product's expected properties and characteristics. Combining various materials to form each component's desired properties could initiate different AM research challenges and opportunities (Oladapo *et al.*, 2019a,b; Tafaoli-Masoule *et al.*, 2019; Li *et al.*, 2017; Ahn *et al.*, 2012). The basic requirements to address these challenges are developing standardized national testing centers to test and improve the AM method. These testing centers could be challenged with the responsibility of developing design and testing policies for AM. Although the finite element analysis (FEA) adopted for the AM primary process analysis and testing is considered an acute phase. The development of modelling and simulation tools for AM technology software cost modeling and new production planning manuals for vehicles, biomedical space and space has currently been investigated (Oladapo *et al.*, 2018a; Jiang *et al.*, 2013). These are to ensure that research, development, and trade produce new material that combines unusual characteristics to produce advanced and complex consumer products. Therefore, monitoring the use of AM technology with composites and nanocomposites have

Table 1 Analysis of the state of materials and working principles of various AM processes

State of materials	Process	Layer creation method	Typical materials	Applications
Powder	EBM	Electron beams scanning	Metal	Tooling, functional parts
	3D Printing	Drop-on-demand binder printing	Polymer, metal, ceramic, other powders	Prototypes, casting shells, tooling
	SLM	Laser scanning	Metal	Tooling, functional parts
Filament	FDM	Continuous extrusion & deposition	Thermoplastics, waxes	Prototypes, casting patterns
	Robocasting	Continuous extrusion	Ceramic paste	Functional parts
Liquid	SLS	Laser scanning	Thermoplastics, waxes, metal & ceramic powder	Prototypes, casting patterns, metal and ceramic
	SLA	Laser scanning	UV curable resin, ceramic suspension	Prototypes, casting patterns
	MJM	Inkjet printing	Acrylic plastic, wax	Prototypes, casting patterns

Note: Tofail, S.A.M., Koumoulos, E.P., Bose, A.B.S., Donoghue, L., Charitidis, C., 2018. Additive manufacturing: Scientific and technological challenges, market uptake and opportunities. *Mater. Today*, 21, 22–37. Oladapo, B.I., Oshin, E.A., Olawumi, A.M., 2020a. Nanostructural computation of 4D printing carboxymethylcellulose (CMC) composite. In: Thomas, S. (Ed.), *Nano-Structures & Nano-Objects*, vol. 21, Elsevier. Article 100423. Oladapo, B.I., Daniyan, I.A., Ikumapayi, O.M., Malachi, O.B., Malachi, I.O., 2020b. Microanalysis of hybrid characterisation of PLA/chA polymer scaffolds for bone regeneration. *Polymer Testing*, 83, Article 106341. Oladapo, B.I., Zahedi, S.A., Ismail, S.O., *et al.*, 2020c. 3D printing of PEEK–chA scaffold for medical bone implant. *Bio-Des. Manuf.* 1–6. Oladapo B.I., Adebisi Aderogba V., Ifeoluwa Elemure E., 2019a. Microstructural 4D printing investigation of ultra-sonication biocomposite polymer. *J. King Saud University - Eng. Sci.* 10. doi:10.1016/j.jksues.2019.12.002. Oladapo B.I., Zahedi S.A., Adeoye A.O.M., 2019b. 3D printing of bone scaffolds with hybrid biomaterials. *Compos. Part B: Eng.*, 158 (1), 428–436.

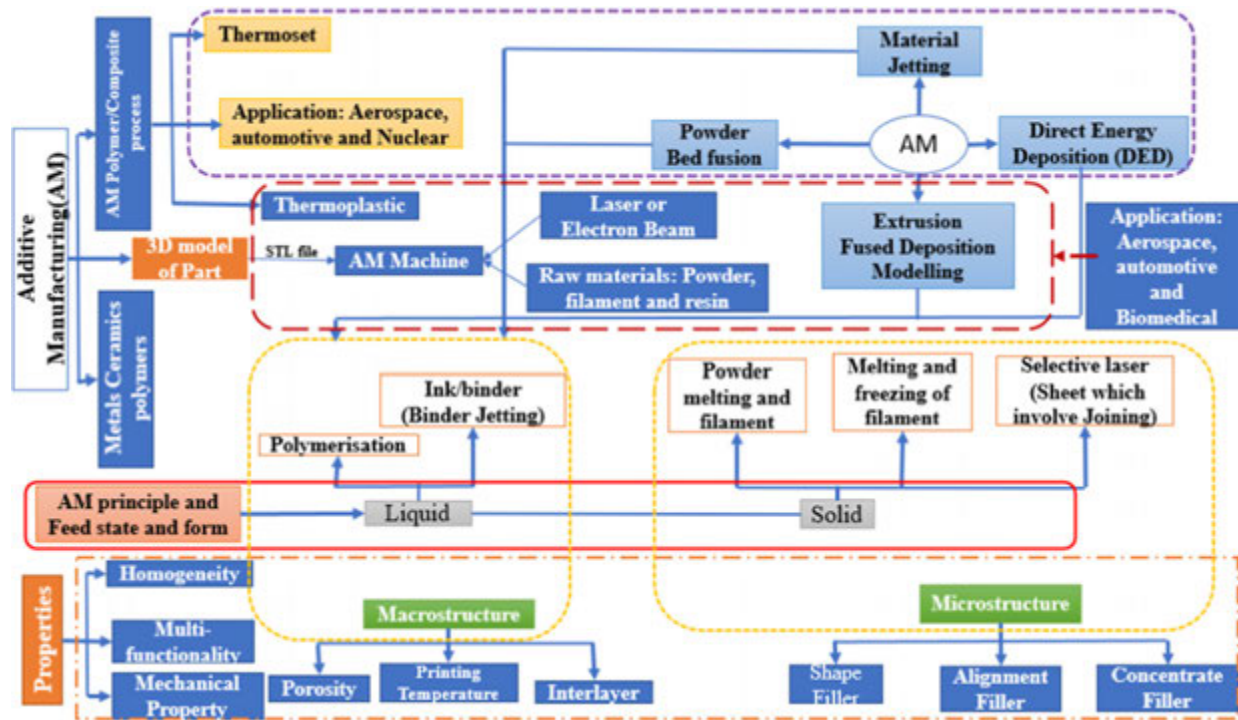


Fig. 1 AM technological steps for polymer matrix composites.

become research of necessity. Moreover, there are few ways products are produced by AM technology with various prototypes, concepts, and functions proposed by many systems over the last 30 years.

Stereolithography (SLA) depends on the solidification of the liquid photopolymer, using an ultraviolet light intensity beam to form a two-dimensional layer line (Oladapo *et al.*, 2018b; Ioana *et al.*, 2018). After completing the first layer, the construction platform moves in the z-direction to create a new photopolymer coat. There are laser sintering, laser melting, fusion forming, multiple electron beam jets, rolling object production, and 3D printing of plaster (Oladapo *et al.*, 2020a,b,c; Exner *et al.*, 2007). A laser-shaped liquid is formed by the deposition of formed metal and 3D impression per head of inkjet powder. There are many ways to implement and deploy AM in the industry. Some of these include small-scale economic production, ecological sustainability, component functionality, and geometric freedom. Research and commercialization of AM technology and materials are now one of the primary fields that have been investigated in the last decay (Kumar, 2009; Vaucher *et al.*, 2002). AM has many essential applications in automotive, aerospace, energy, biomedicine, bone implant, and other areas. Fig. 1 shows the order of phases of AM technology from the abstract design to the implementation stage. There are many requirements of AM technology in several active areas. For example, studies on research aimed to investigate AM technology through different types of composite materials for bone implant have been conducted (Oladapo *et al.*, 2019b; Slocombe and Li, 2001) the importance of biomedical engineering. These research include: (1) verification of the physics and properties of AM models, (2) adapting health products to improve the health of the population, (3) apply monitoring techniques, such as sensors to measure and monitor AM operations and (4) increase demand-to-demand efficiency by simplifying the supply chain system.

However, there are various AM techniques, but some are used to develop composite materials. The processes used to make composite materials are necessarily laser selective sintering or fusion modeling network. In some AM techniques, the fiber-reinforced compounds were produced. AM techniques mainly used in fiber-based compounds are SL, FDM, and SLS. Considering suitable powder-based techniques, such as rapid prototyping (RP), the blend is made into soft powder, challenging to extract the fibre layers (Hon and Gill 2003; Cheung and Gibson 2002). It is worthy of note that the inclusion of short fibres in the process is complicated, and the use of prolonged or continuous tissue is limited only by SL (Srinivas *et al.*, 2009; Shishkovsky and Tarasova, 2001). AM processed FDM and Laminated Object Manufacture (LOM) strips of suitable filament fibre-reinforced composite, as a precursor before, require laminated materials. Therefore, it must be formulated and developed.

AM Applications

The addition and improvement of the printed products' value-adding characteristics are seen as good benefits in employing AM technology. This section subsequently explains the most common products made using AM technology in diverse areas (Alexandre and Vogt, 2004; Oladapo *et al.*, 2019c).

Fused Deposition Modeling

FDM can produce durable composites by melting some or all the fibres formed from the raw material, creating a link between the layer and the continuous layer. There should be a removable wax support structure in protruding parts, using the second nozzle to deposit the support materials. The development of raw materials for FDM production is essential. The filament of the raw material must have sufficient composition, strength, and low viscosity. The base polymer, which consists of basic polymers, plasticisers, and surfactants and other metals, polymers, and ceramics, is forced out like a filament through the nozzle during the process. Glue is usually applied to the base plate. The glue is a solution to increase the surfactants' adhesion and elasticity, increase the flowability, and permit homogeneous metal distribution as the build-up progresses. The filament development requires the proper mixing of these components, which give a useful ability for a bone implant (Yu and Schaffer, 2009; Czyzewski, 2009).

The main reason for treating composite materials on a single element is facilitating the liquid phase sintering process using different materials to obtain the alloying materials' inaccessible properties. The first type of copper (Cu) acts as a molten liquid during the Process and contains SLS Fe-Cu bound to the Fe powder to form Fe-Cu compounds. The development of mechanical properties or other properties of steel products is similarly possible. The formation of common compounds using another type of SLS/SLM process is carried out by adding hydroxyapatite (HAP) to polycaprolactone (PCL) to form PCL/HAP through SLS to increase resistance and biocompatibility and use for a bone implant (Klosterman *et al.*, 1999; Zhan, 2001). The production of such composite materials in the SLS/SLM domain, using the three methods is discussed in the following section.

Composites Production

The most surprising application is forming a polymer matrix composite (PMC), and the coupling mechanism is a blended and incinerated liquid phase invasion, polymer, and ceramic powder. PCL and HAP, polyetheretherketone (PEEK), and HAP (Oladapo *et al.*, 2019c; Karalekas, 2004) (Fig. 2) and monotonic polymethyl methacrylate (PMMA) have been used to generate a laser, and they show the best combination of powder. However, powder coatings are used for biocompatibility (Adeoye *et al.*, 2017; Gupta and Ogale, 2004). There are also other advantages of powder coating, in the case of nano- Al_2O_3 and - pressure-sensitive nanoparticles compound Al_2O_3 to avoid the accumulation of the nanoparticles to provide the particle dispersion and coated with pressure-sensitive adhesive (PSA) tape. The appropriate polymer matrix is used as a doping agent, instead of reinforcing it. This is so because it forms fibres in the presence of the challenge of a loose powder layer (Zak *et al.*, 2000; Balogun and Oladapo, 2019). A stirred auxiliary powder polymer's density and strength are not suitable for maximizing the powder particles' use. The dust can be used for glass powder coated polyamide (PE), aluminium powder, and high-density polyethylene (HDPE)/HA-coated will help each particle to correct the problem and compound components that are distributed to the final products. However, when the powdered ingredients are fibers, production problems arise (Cijun Shuai *et al.*, 2020; Selvam *et al.*, 2020). In this method and with a ceramic matrix of carboxymethylcellulose (CMC), metal matrix (MMC), (used in the preparation of materials in general), ceramic products and SLS metals do not produce deposition due to the quality of products and change in the material compositions (Ashish *et al.*, 2020; Florina *et al.*, 2019). For solid materials, such as PMC (for complete cure), the powder mixture is added to additional materials or filtered porous products. The addition of LaCO_3 to WC-Co and Cu components helps to reduce internal stresses build-up of the material. Surface strength strengthens both products, and Green CO can be obtained by the infiltration of bronze (Park *et al.*, 2017; Florina *et al.*, 2019). Fig. 2 shows a fabrication process and technique adopted for 3D-printing and testing of PLA, HAP, and PEEK for biomedical applications. Table 1, as previously presented, summarizes the materials directly employed by SLS DuraForm Customers fiberglass and synthetic, and the Form AF (fiber), has many specific compounds, synthetic, and Aluminum added to their composition (Rebelo *et al.*, 2017; Shuai *et al.*, 2020).

Fig. 3 shows a fabrication process for the development of smart soft composites and a 3D-printed morphing structure for phone/robot.

Composites of In-Situ Reactions and Furnace Treatment

Laser-induced chemical reactions are used to produce particles on-demand in SLS. The energy from this system by the laser beam can be used in two different ways: (1) to overcome the start energy of the reactants during the reaction stages and (2) to form chemical compounds during the mixed reaction. In-situ formation and uniform distribution of enhanced wetting compounds are better than the sclerosis of compounds to release exothermic energy contributing to the chemical mixture. Examples of the first type are the formation of TiB_2 and MMC supplemented with TiC in a mixed powder of Cu, Ti, and B_4C (Isakov *et al.*, 2016; Czyzewski, 2009). The second type is, for example, a self-leveling high temperature (SHS) synthesis of TiC-A1203 in a compound of TiO_2 , Al, and C, CuO, and Al are compound of Al_2O_3 -Cu and NiTi-HA is a composition of NiTi and HAP. The chemical reactions can also contribute to forming a binder in treatment with SiC laser, decomposing the SiC, and then reacting Si_2 with the O_2 gas connected to the remaining SiC powder (Srinivas *et al.*, 2009). A sintering treatment in a laser oven is another way to prepare a compound where the furnace can be used. Before opening the furnace or after penetration, the chemical reaction of the furnace and infiltration, which is an example of first type sintered acrylic laser glass, is processed in an oven that dissolves the acrylic binder and the glass in the ceramic apatite and mullite phase of $\text{fSiO}_2\text{AlO}_3\text{-P}_2\text{O}_5$ partially substituted CaO-CaF_2 ceramic compound (Kurimoto *et al.*, 2015; Motealleh *et al.*, 2018).

In this case, the compound was prepared using an oven cycle without filtration, and Al furnace was filtered with a sintered laser coated with SiC powder polymer to form the MMC. Other examples include the higher melting temperature of Cu-Mo formation of the compound at a high temperature of ceramic superconducting, which has guanine, In_2O_3 , and the infiltration of SiC (Shemelya *et al.*, 2015; Oladapo *et al.*, 2020a,b,c). The second type, the most common, is the formation of Si/SiC compounds.

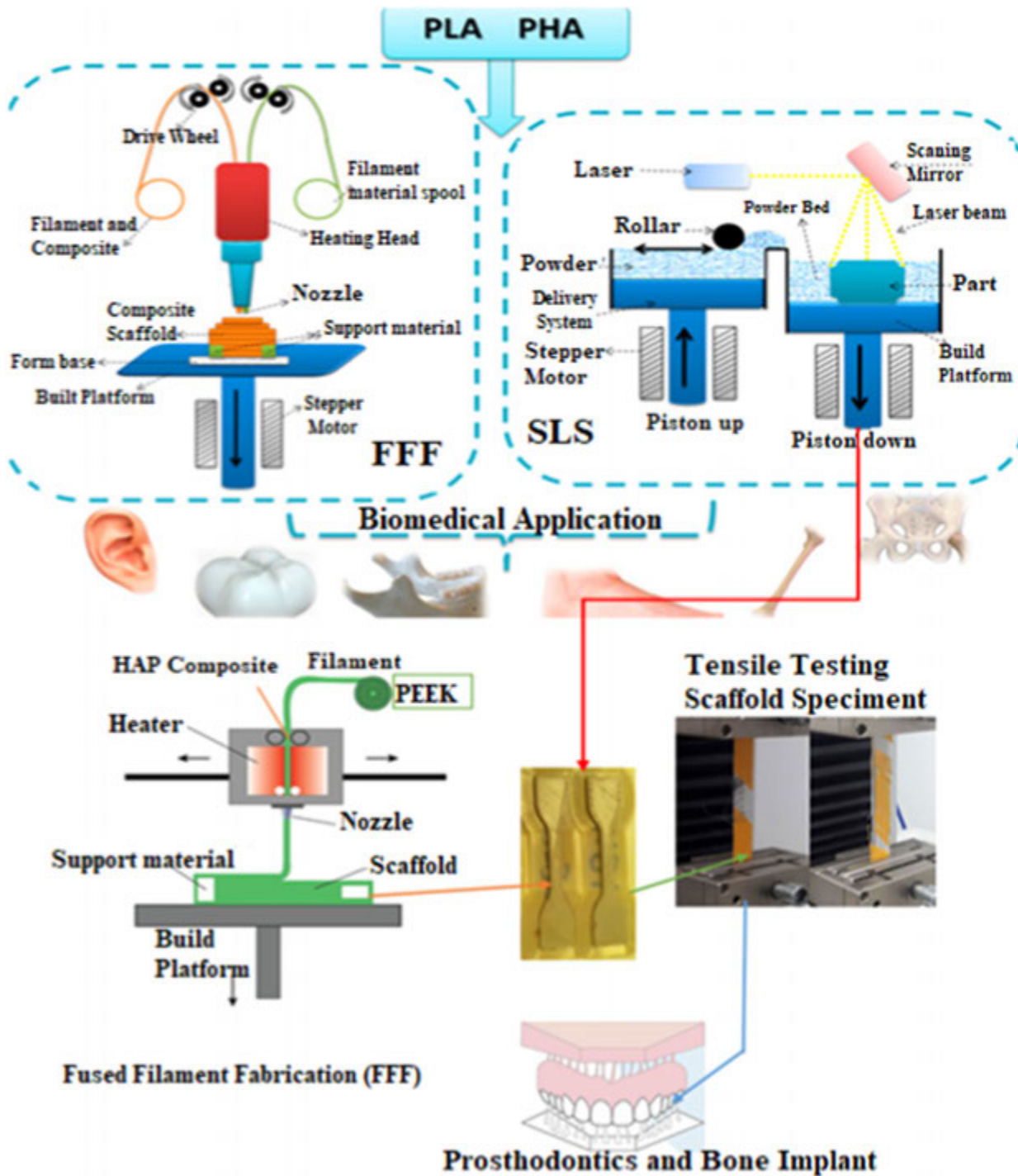


Fig. 2 3D-printing and testing techniques of PLA, PHA, and PEEK for biomedical application. Reproduced from Rebelo, R., Fernandes, M., Figueiro, R., 2017. Biopolymers in medical implants: A brief review. *Procedia Engineering* 200, 236–243. Florina, D. Cojocaru, V.B., Popa, M.I., Lobiuc, A., Verestiuc, L., 2019. Biopolymers – Calcium phosphates composites with inclusions of magnetic nanoparticles for bone tissue engineering. *Int. Jou. of Bio. Macromol.* 12515, 612–620.

Laser treated SiC is treated with a phenolic resin. After curing in the furnace, the resin causes the carbon with a part of the infiltrated Si's made to react to form SiC and finally produces the Si-SiC compound. The amount of SiC in the compound can be controlled by transforming the green product with the phenolic resin. Another example of a chemical reaction located in a furnace is nitrogen gas that reacts with the Al alloy's green product to form AlN. Then, the MMC is made by licking with the Al alloy. The Al compound production with force depends on nitride formation in the nanostructure (Kalsoom, 2016; Castles and Isakov, 2016).

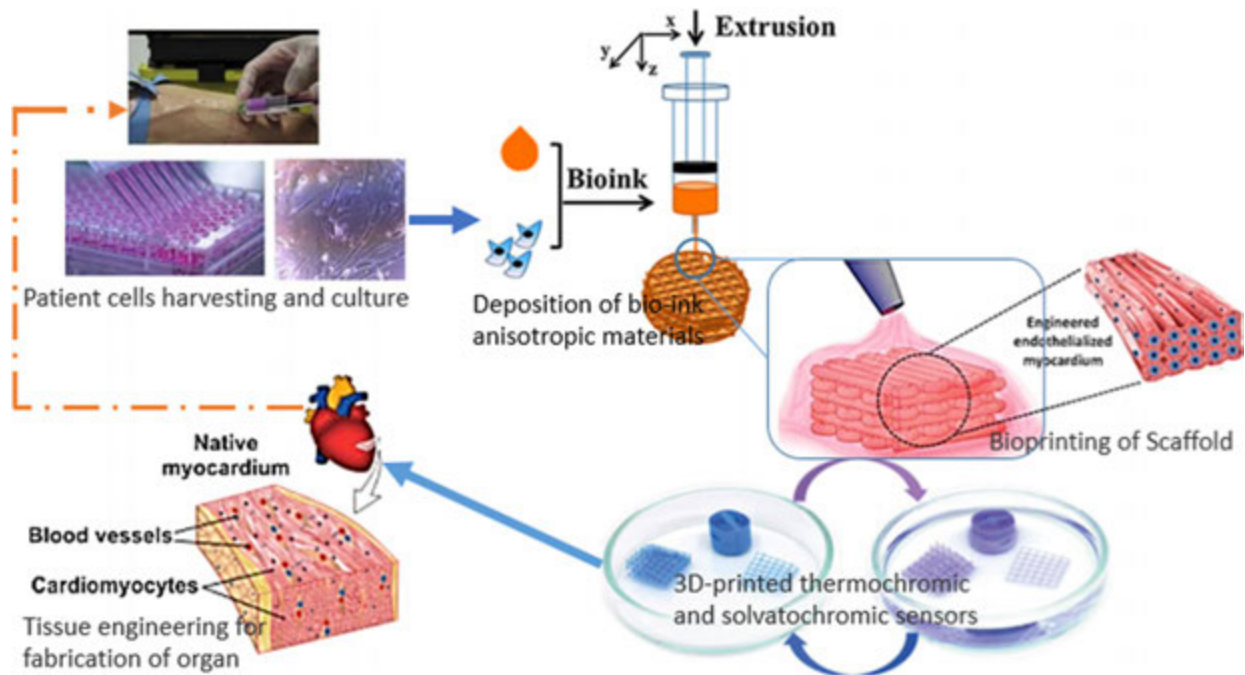


Fig. 3 Patient cells harvesting and culture Fabrication process for developing smart soft composites 3D-printed morphing structure of solvatochromic sensor for organ production.

Polymeric Products

Production of polymer products with AM is called high-speed sintering (HSS). The main application of polymers by AM is the production of polymer prototypes used for visual verification and assembly approval. The polymers can also be used in biomedical applications through compatible and biodegradable polymers. Compatible biopolymers can be used in external and internal applications in the biomedical field. The hearing aid sector is an example of an appeal globally because of the hardness and durability of the polymer materials used (Isakov *et al.*, 2016; Feng *et al.*, 2019). An example of internal use is a lumbar tissue graft with cardiac graft and microscopic internal cavity. Polymeric materials are also used in art and jewellery projects, as they are used for vacuum leak modeling.

Furthermore, one of the best metal applications of AM technology is the AM motor design. The general concept of mould manufacturing can produce more complex free-form cooling channels than the heat holes obtained from drilling. AM technology's application generally ensures consistent heat transfer and adjustable heat dissipation (Hwang and Reyes, 2015; Perez *et al.*, 2014). Usually, it is used for laser or electron beam applications, especially during the production of images. Hybrid, ready-to-shape shapes are easy to add, save time, cost, and enhances processing capabilities. In addition to using metal to create LS, it has a more detailed profile, especially in biomedical areas of bone structure, which are essential applications. Also, computed tomography (CT) speeds up general biomedical products and not through conventional methods, such as scanning, modifying, converting to STL files, cutting, and production, which are more comfortable. Another advantage is reducing operating time (Saravanan *et al.*, 2016; Kokkinis *et al.*, 2015). Fig. 4 shows an example of computed tomography in the biomedical field, as previously presented.

The metal AM has three different material processing categories, depending on the AM method, building volume, and power source. These categories include bedding systems, power distribution systems, and wire feed systems, shown in Fig. 5. Another classification of the AM metal process depends on the method of binding the metal particles. For example, the Direct Metal Deposition (DMD), fabrication processes, as shown in Fig. 5. The examples of things used in AM mixed processes are SLS, 3DP, FDM, and SLA, while SLM techniques used models for LMD and CPA (Martin *et al.*, 2015; Zhong *et al.*, 2001). From Fig. 4 it can be observed that composite AM technologies can be classified based on the composite materials available for specific application/production and its tendency for further development. Also, Fig. 5. shows the classification of metallic powder that can be adopted and currently in use for AM processes.

Standards for Polymers Testing

The American society for testing and materials (ASTM) standards for plastic testing include ASTM D638 for tensile testing. Examples are the tensile test of a dumbbell-shaped specimen in the thickness direction. During this test, the general properties are tensile strength, elasticity, rupture flexibility, and elasticity modulus. ASTM D412 is designed for tensile testing of vulcanized rubber and thermoplastic elastomers that could be adopted for AM (Ning *et al.*, 2015; Love *et al.*, 2014). The ASTM D882 standard includes tensile the sting for thin plastic films. Also, ASTM D3039 covers the extension properties of polymer matrix composite materials reinforced with high modulus fibers. The international organization for standardization (ISO) developed the ISO 527

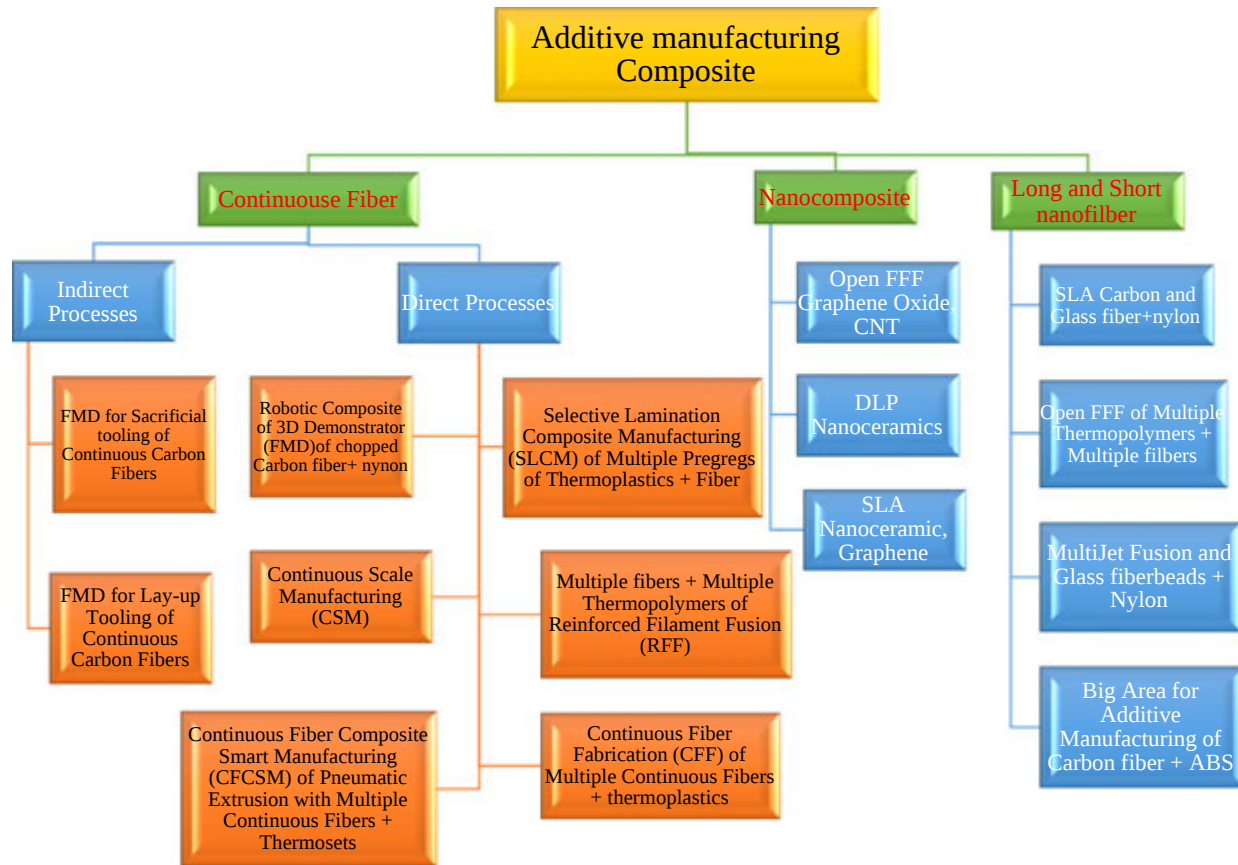


Fig. 4 A summary of the AM technologies and their composite materials for application/production.

standard to characterise plastic traction. The ISO 37 standard also deals with obtaining the tensile properties of thermoplastic and vulcanized rubbers (Saravanan *et al.*, 2016; Feng *et al.*, 2018). ASTM D790 addresses the determination of flexural properties, including flexural strength and plastic flexural modulus. There are two methods used to determine these characteristics: Method A is for materials that are broken by small deviations, while Process Up is for elements with significant differences (Chen *et al.*, 2018; Lian *et al.*, 2019). ISO 178 deals with the method to determine the flexural properties of rigid and semi-rigid plastics. Also, this pattern provides the parameters of flexural strength and flexural modulus. The ASTM D1938 covers the standard for determining a plastic film or film's tear resistance or film of comparable thickness. This standard does not apply to fragile plastics. ISO 34 has ISO 34-2: 2015; this refers to the breaking test standards for small samples and ISO 34-1: 2010 for angled traction, crescent, and pants. ASTM D695 covers the compression test of hard plastics, and the obtained properties include the compressive strength, modulus of elasticity, yield stress, and tension, in addition to the yield strength. The deformation rates used are relatively low (Rizwan *et al.*, 2017; Sadeghzade *et al.*, 2017) for ISO 604 used as the test model. The ASTM D256 for Izod impact test and ASTM D6110 for Charpy impact tests measure plastic samples' impact resistance with pendular hammer notches. International Standard Organization also has similar standards for impact test samples for Izod and Charpy impact tests. ASTM D7791 covers the measurement of the fatigue properties of plastic materials under uniaxial loading. In general, universal test machines are used for this method. ASTM D3479 deals with tensile fatigue tests of polymer matrix composites (Ning *et al.*, 2015; Sun *et al.*, 2017).

Nanocomposites

It has been elucidated that more concern is vital to produce composite materials in a single process cycle. This is one of the possibilities of additive technologies to meet the above requirement in using nano-moulding structures of building materials. It has been confirmed that the composite structure of 3D nanomaterials has many applications in chemical and biological environments. For instance, SLS has the advantage of producing functional components of metal connections with less labour, time, and skills to produce the geometry of internal states or complexity (Raz *et al.*, 2018; Ain *et al.*, 2017). The effect of SLM process variables is investigated by the microstructure of the components produced due to nano-carbide, titanium carbide (TiC) production fields for general properties, and metallurgical mechanism. It is formed without sufficient laser energy or interlayer; the condensation reaction is limited for a small extension in a lens stored in the Ti6Al4V + 20% TiC/Ni.



Fig. 5 Classification of metallic powder used in additive manufacturing processes.

Thermogravimetric and spray drying processes are new techniques that combine nanocomposite coatings with the flow characteristics required to meet the requirements. As shown in Fig. 6, additive nano-manufacturing (ANM) can select different materials and have more flexibility in the project. Examples include immersion lithography techniques: ANM, dip-pen nanolithography (DPN), magnetic hydrodynamic jet clip (MHD), optical tweezers, and electrokinetic nanomanipulator. The primary variable, ANM, has a minimum value and a choice of process rates. Materials comparison of several technologies: It was concluded that the mechanical properties, thermal and electrical conductivity, sintering temperature, and nanocomposite access could be increased by studying ANM properties' AM technique, as shown in Table 2. In every method, AM still faces some obstacles (Lin *et al.*, 2018; Oladapo *et al.*, 2020a,b,c; Cui *et al.*, 2020).

The printing's combination attracts rough surfaces on the printed parts and nozzle clog during the printing process. In other words, the method for determining the processing, synthesis patterns of nanomaterials and processes is not sufficient (Oladapo *et al.*, 2020a,b,c; Lian *et al.*, 2019). One nanocomposites fabricated through AM technology is nanocomposite TiC/Ti, using the SLS effects and the nanoscale type. The structural properties of SLS fabricated TiC/Ti include microstructure condensation, mechanical, and nanocomposites. Using mixed nanoparticles and TiC/Ti, it can then be summarized, as coated with mechanical and nanocomposites, then covered with coated TiC/Ti. Essential factors affected the concentration. The laser has a maximum power of 0.33 kJ/m. TiC/Ti nanocomposite, which focuses on microstructure, was added to the TiC of the nanostructures. SLM is responsible for the morphology of the density and SLM nanoparticles, maybe a relatively dense microstructure of the susceptibility process. The TiC, 0.22, and 2.8×10^{-6} m low laser friction coefficients can be additional parameters, due to the high-intensity wear rate (Love *et al.*, 2014; Oladapo *et al.*, 2018a)

Structural Composites

Periodically, titanium and titanium cell structures with a wide range of biomedical applications require the production of computer-aided design/manufacture (CAD/CAM) layers in EBM processing techniques used in medical-grade production

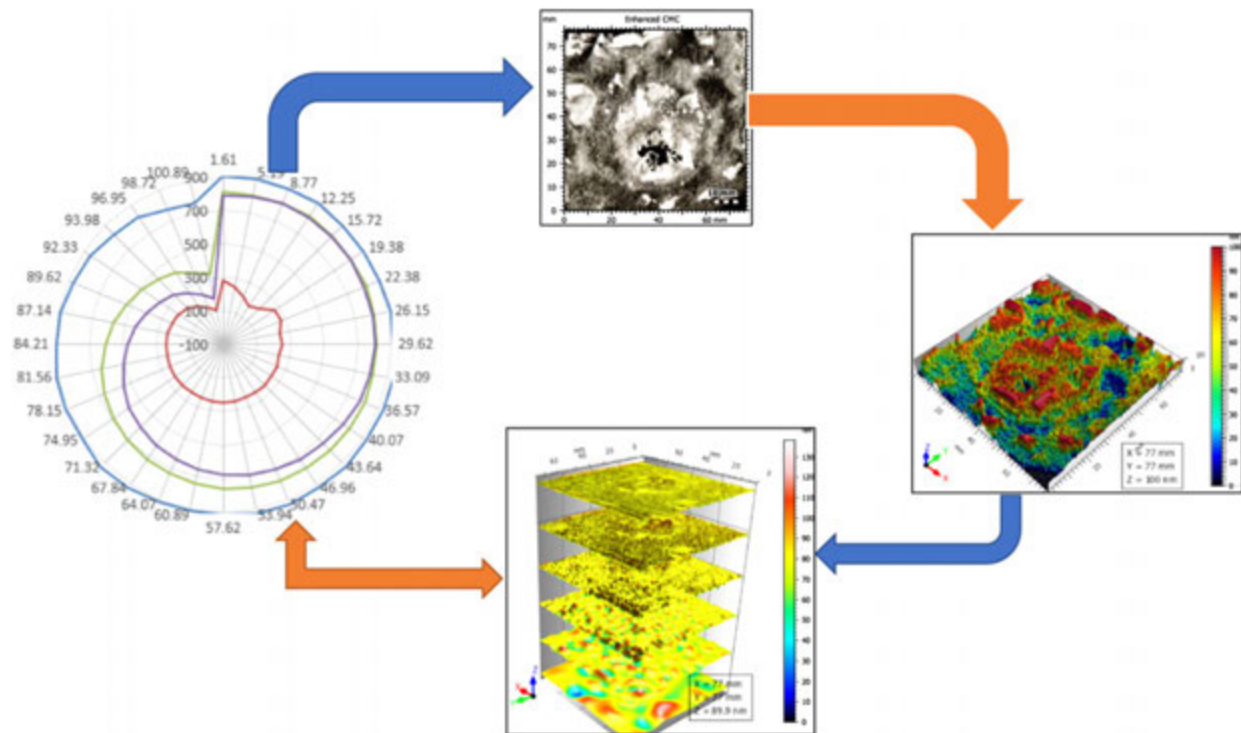


Fig. 6 SEM and the relative nanostructure processes of computational 4D printing of CMC and its composite.

Table 2 Comparison between different ANM technological features

Method	Material	Resolution	Speed
EHD	Metal nanoparticles, polymers, block copolymers	10 nm	80 mm/s
STM	Single atoms (e.g., Xe)	Atomic	<1 nm/s
DPN	From small organic molecules of biological polymers and form colloidal particles to metal ions and sols	50 nm on polycrystalline surfaces, 15 nm resolution on single-crystal surfaces,	Increased with the number of probes.
DLW	Polymers, metals	65 nm, 22 nm	100 lm/s
AFM	Single atoms of nano-scale object (CNTs, nano-particles)	Atomic	<10 nm/s

Note: EHD, STM, DPN, DLW and AFM represent electrohydrodynamic, scanning tunnelling microscopy, dip-pen nanolithography, direct laser writing, and atomic force microscopes, respectively.

substitutes. Due to the need for real-time conditions, titanium cell structures' mechanical properties are suitable for medical applications. To study the scaffold's feasibility and performance, it was produced in one step using both a laser powder and a wire feed. The materials used in this study are copper powder and nickel wire for the accumulation of copper/nickel/iron structure in H13 tool steel - the distributions of elements related to the morphology, microstructure, appearance phase. They are examined under a scanning electron microscope (SEM), spectroscopy, energy distribution (EDS), X-ray diffraction (XRD), and scanning electron microscope. Cu-Ni precipitation at a second powder approves with gradients and sedimentation functions. Another important concept that has been developed is mixed metals. The laser deposition process has a significant advantage, in that a puddle of fusion is formed after the laser, which makes it very convenient to coat the layer by alloy. This characteristic allows for separate composition properties for each level. Traditional methods hinge on localised thermal treatment, but laser deposition (LD) allows the installation and assembly of hardware freely through computer models, resulting in controlling the internal structure's composition. This research is most useful in studies of metal metallurgy and alloy development. **Fig. 7** shows the design of the ear and a composite graduated alloy during LD processing.

The functionally graded material (FGM) suggests the opportunity to regulate the arrangement and enhance the installed part's properties. FGM has many potential applications. Possible FGM examples; thermoelectric and dielectric classes are piezoelectrically classified materials, grade composite electrodes, and tungsten-copper compounds. **Fig. 7**. Shows a representation of 3D interweaving of biology and electronics via AM to generate a bionic organ and 3D bioprinting process from the design stage to control deposition module. With three different head of tissue for human organ, the 3D model is generated from the patient's medical image using computer tomography for precision Multi-Cathedral. The CAD bionic ear of optical images of the functional

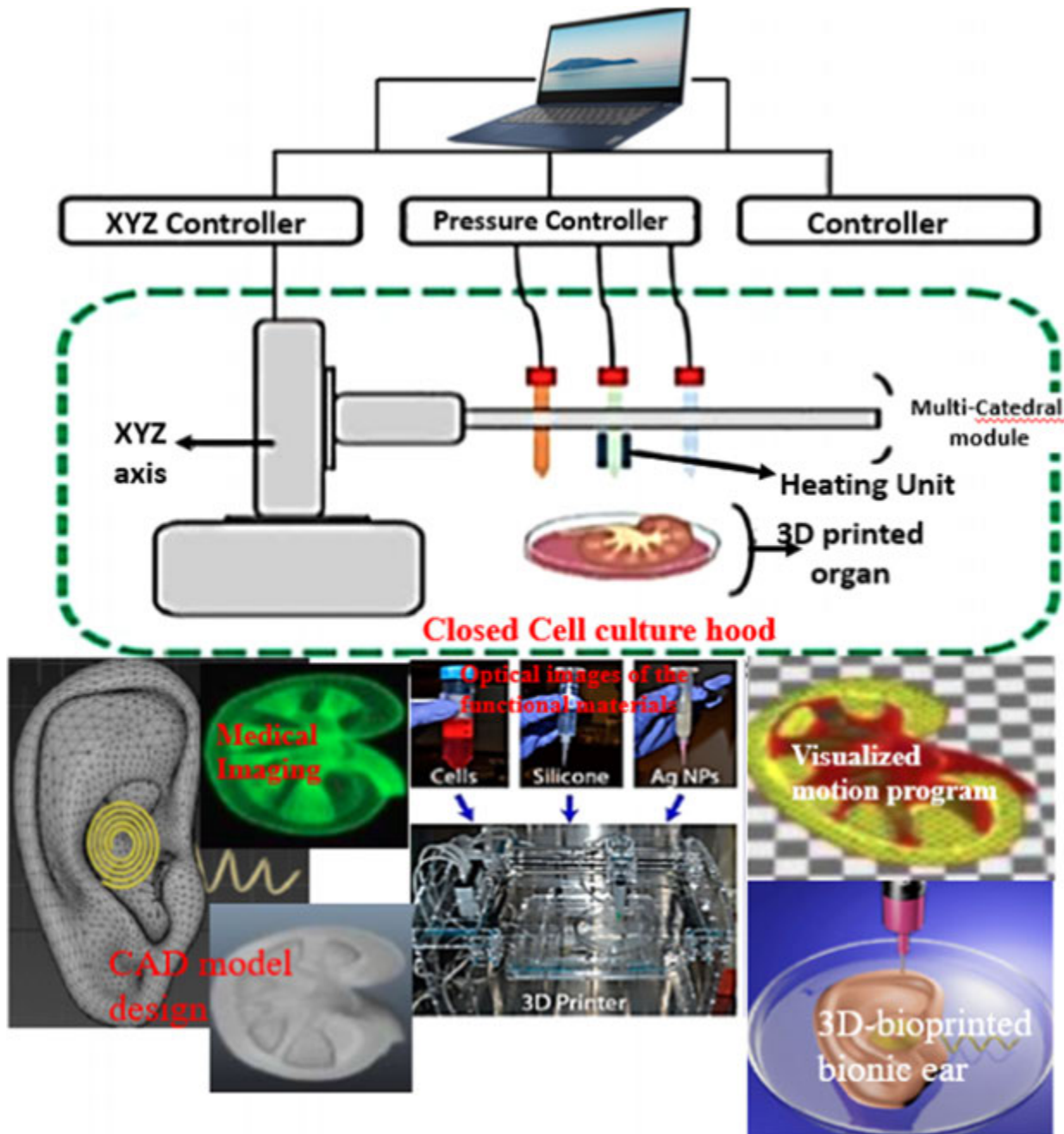


Fig. 7 3D interweaving of biology and electronics via AM to generate a bionic organ and 3D bioprinting process from the design stage to control deposition module with three different head of tissue for human organ, 3D model generated from the medical image of the patient using computer tomography for precision. The CAD bionic ear of optical images of the functional materials, AgNP infused silicone for the bionic ear and 3D printer for the printing process illustration of the 3D-printed bionic ear (Jiang *et al.*, 2013; Shuai *et al.*, 2020).

materials, AgNP infused silicone for the bionic ear and 3D printer for the printing process illustration of the 3D-printed bionic ear (Jiang *et al.*, 2013; Shuai *et al.*, 2020).

Metal or metal-ceramic FGM, SLM technique, and laminated objects can be done by laser coating or high solidification. It can be done using printing processes by polymer-polymer or polymer-ceramic, ceramic-ceramic, inkjet printing, SLS, or 3D (Shuai *et al.*, 2020; Selvam *et al.*, 2020). One technique used to produce fully dense structures through functional classification is laser deposition, where various compositions are injected. Nanocomposite-based FGM also has sufficient potential. For practical grade nanocomposites, the 3D structure is fabricated using free-form fabrication based on SLS fabrication. In this study, nanocomposite nylon-11/silica is prepared using different volume fractions of the fumed silica nanoparticles of 15 nm in the range of 0%- 10%. The hardness is between 17.8 and 19.2 GPa and is slightly below the boundary between adjacent layers. The upper surface's

toughness increase is due to the transition phase from t-ZrO₂ to m-ZrO₂ during the lower surface fracture. One of the FGM studies focuses on the Al and Cu coupling of stainless steel plates, using ultrasonic consolidation (UC) bonding techniques. The optimized layer sequence is adopted, and it is found that the optimal sample 62 had a 200-sheet width and a 1300-length. The optical microscopy card shows that UC FG Musing is successfully produced. In this study, the final recommendation to improve the FGM production process using UC is to adopt the processing strategy or use an intermediate layer (Sadeghzade *et al.*, 2017; Isakov *et al.*, 2016). With EBM metal processing, dense and porous dusty titanium structures are produced to meet the aesthetic and functional requirements of patients and surgical patients.

Laser Net Shaping

Laser Network Modeling (LEM) is similar to SLS because it is a powder and laser technology. More than two critical steps attract the accumulation of dust. The production of composite materials in the laser engineered net shaping (LENS) is similar to SLS lasers and powder's reaction. The lenses can be dust-free. Lenses are used to form compounds having different strengths and produce FGM, using different powders. Also, in composite LOM fibre-reinforcement, there is an example of the production of a fibre-reinforced composite (FRC) film of 0.5 mm fixing the layers of ceramic strips with pre-prepared fibres. The fiber preparations are made by connecting a unidirectional continuous fiber to a thermosetting resin (Vaucher *et al.*, 2002; Rizwan *et al.*, 2017). Continuous ceramic fibre cutting with CO₂ laser is damaged during the LOM process due to combustion heat and adjacent polymers. The problem can be avoided using a copper vapour laser because the fibre is disturbed by the photoelectric mechanism. The LOM product is also developed by linking the cellulose fiber pyrolysis filter paper to adhesive tapes developed from phenolic resins, polyvinyl butyral, benzyl tantalate paste containing butyl and ethanol. The phenolic resin is changed to carbon by producing the pyrolyzed part under nitrogen at 800°C. Porous carbonized samples were then filtered through liquid Si at 1500°C under vacuum to produce FRC (Kumar, 2009; Feng *et al.*, 2019).

SLS and FDM of Fiber-Reinforced Composites

Among all the AM techniques, selective SLS laser sintering is frequently used with short fiber, continuous fiber, and fibre mats in FRC. The choice of fiberglass instead of ceramic or carbon fiber reduces ultraviolet rays' opacity, which is very suitable for SL technology for FRC production. Although continuous filaments are ideal for improving mechanical properties, shorter fiber mixtures with higher aspect ratios have similar properties (Du *et al.*, 2019; Pourhaghgouy *et al.*, 2016). An increase in the volume leads to an increase in the functionality, but it is limited and attracts additional challenges after creating and processing the scene. However, coating the fibers helps to reduce the viscosity of the mixture. The grains also bind between the layers partially in an area not encapsulated in the first layer. Uneven lengths, random alignment of components, and fractures during mixing are possible. Table 3 summarizes some materials used to produce FRC in SLS (Karalekas, 2004; Slocombe and Li, 2001).

Composites for Biomedical Applications

Using the AM technique, scaffolding is used in dental implants to form lean racks and continuous biopolymers. Moreover, it is used to produce ceramics with RP. These compatible compounds are bioactive, biominerals, or at various levels of biological adsorption. Biodegradable compounds stand out as new materials incorporated into tissue engineering, because: (1) no other surgical procedures are required to remove implants after treatment, and (2) less risky mechanical properties between bones and implants (Oladapo *et al.*, 2019b; Park *et al.*, 2017). Therefore, 3D printing techniques for membrane separation is possible through

Table 3 Additive Manufacturing Processes

Material adhesion	Material jetting	Extrusion thermal	Laser based additive manufacturing		Electron beam
			Laser polymerization	Laser melting	
Laminated object manufacturing	Thermojet	Robocasting	Stereolithography	Direct metal deposition	Electron beam
Solid foil Polymerization	Multi-jet modeling	Fused filament fabrication	Solid ground curing	Laser engineered net shaping	
	Particle manufacturing		Liquid thermal polymerization	Stereolithography contour	
	Ink Jet Printing			Layer plastic deposition	
				Selective laser sintering	
				Selective laser melting	
				Direct metal laser sintering	

Note: Florina, D., Cojocaru, V.B., Popa, M.I., Lobiuc, A., Verestiuc, L., 2019. Biopolymers – Calcium phosphates composites with inclusions of magnetic nanoparticles for bone tissue engineering. *Int. Jou. of Bio. Macromol.* 12515, 612–620. Lian, H.X., Liu, Z., 2019. Meng Enhanced mechanical and osteogenic differentiation performance of hydroxyapatite/zein composite for bone tissue engineering. *J. Mater. Sci.* 54, pp. 719–729.

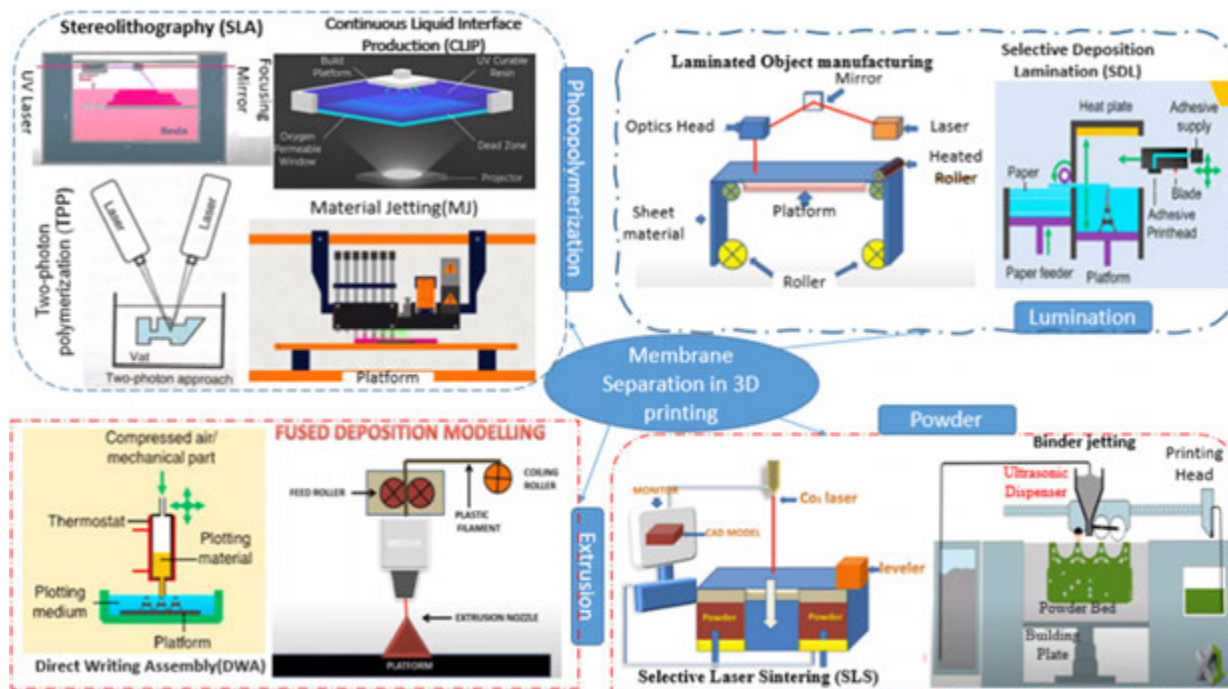


Fig. 8 Photopolymerization of membrane separation through different AM techniques.

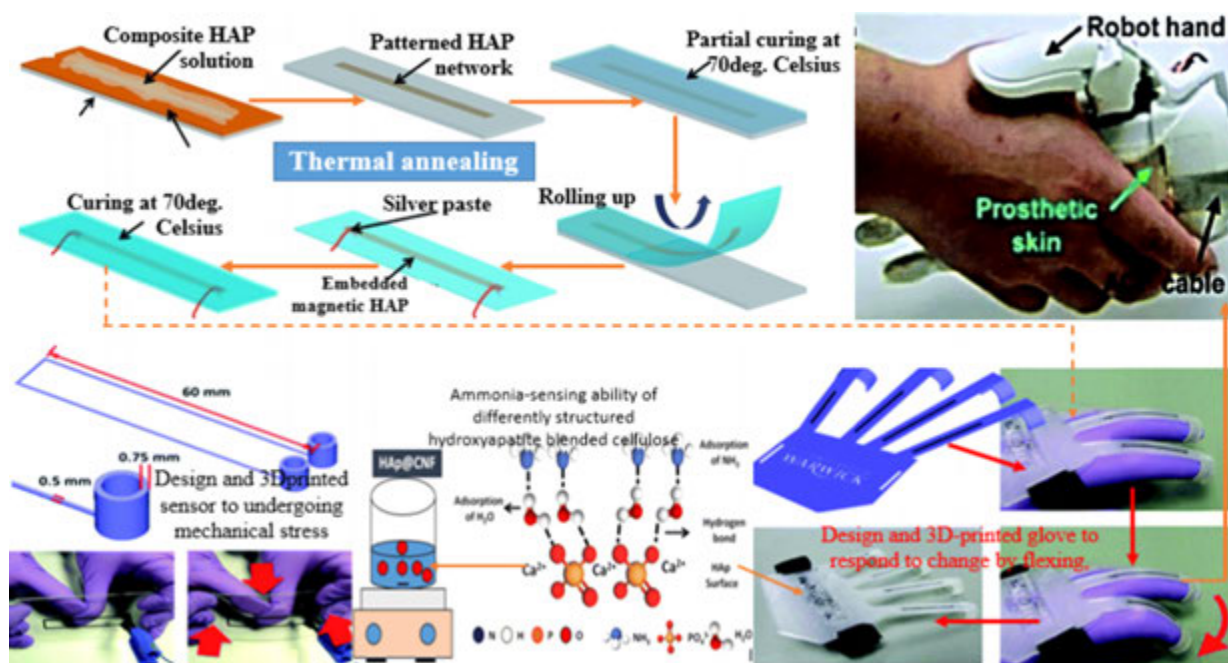


Fig. 9 Flex sensor Design and 3Dprinted sensor to undergoing mechanical stress and glove to respond to change by flexing Emerging flexible sensors based on nanomaterials of recent status and applications and Ammonia-sensing ability of differently structured hydroxyapatite blended cellulose. Reproduced from Leigh, S.J., Bradley, R.J., Pursell, C.P., Billson, D.R., Hutchins, D.A., 2012. A simple, low-cost conductive composite material for 3D printing of electronic sensors. *PLoS ONE*, 7 (11), e49365. Narwade, V.N., Anjum, S.R., Kokol, V., *et al.*, 2019. Ammonia-sensing ability of differently structured hydroxyapatite blended cellulose nanofibril composite films. *Cellulose* 26, 3325–3337. Wen, N., Zhang, L., Jiang, D., *et al.*, 2020. Emerging flexible sensors based on nanomaterials: Recent status and applications. *J. Mater. Chem. A* 8, 25499–25527.

Table 4 Composites fabricated by various AM techniques for biomedical applications

Techniques	Composites	References
SL	PPC, TCP	(Shuai <i>et al.</i> , 2020; Umme <i>et al.</i> , 2016; Lian <i>et al.</i> , 2019)
	DEF, HAP	(Lu and Wong, 2000; Ahn <i>et al.</i> , 2012; Love <i>et al.</i> , 2014)
SLS	PEEK, HAP	(Oladapo <i>et al.</i> , 2020a,b,c; Oladapo <i>et al.</i> , 2019b,c)
	Ni, Ti, Ca ₅ (PO ₄) ₃ OH	(Zhong <i>et al.</i> , 2001; Ning <i>et al.</i> , 2015; Kokkinis <i>et al.</i> , 2015)
	PVA, HAP	(Shuai <i>et al.</i> , 2020; Hwang and Reyes, 2015; Karalekas, 2004)
	HDPE, HAP	(Perez <i>et al.</i> , 2014; Saravanan <i>et al.</i> , 2016; Hwang and Reyes, 2015)
	PA, HAP	(Oladapo <i>et al.</i> , 2019c; Park <i>et al.</i> , 2017; Czyzewski 2009)
	PE, HAP	(Florina <i>et al.</i> , 2019; Rebelo <i>et al.</i> , 2017; Martin <i>et al.</i> , 2015)
	PCL, HAP	(Vaucher <i>et al.</i> , 2002; Hon and Gill, 2003; Slocombe and Li, 2001)
	PLLA, HAP	(Oladapo <i>et al.</i> , 2020b; Ioana <i>et al.</i> , 2018; Bikas <i>et al.</i> , 2016)
LOM	Ca ₃ (PO ₄) ₂ -glass, HAP	(Yu and Schaffer, 2009; Klosterman <i>et al.</i> , 1999)
3D Printing	PLGA, TCP	(Cheung and Gibson, 2002; Srinivas <i>et al.</i> , 2009; Zhan, 2001)
FDM	PP, TCP	(Shishkovsky and Tarasova, 2001; Alexandre and Vogt, 2004)
	PCI, HAP	(Exner <i>et al.</i> , 2007; Tofail <i>et al.</i> , 2018; Kumar, 2009)

various methods, as depicted in Fig. 8. AM presents the following unique advantages in conventional building techniques: it explains more about its approval, considering shape and size, freedom, and spherical pore formation. With no toxic binders or solvents, accuracy, and repeatability, various sizes and shapes are few parameters required to create RP-racks, using traditional techniques (Rebelo *et al.*, 2017; Oladapo *et al.*, 2019c).

AM creates necessary local pores to create a potential field for tissue growth in general techniques, creating a prescribed global protozoon. Central follicles are used to disperse food, blood flow, and fluids and control cell growth and tissue differentiation. The addition of Ca-P ceramics to polymers forms compounds. Better adhesion behavior of similar bones and untreated polymers is obtained. Calcium phosphate increases the biodegradability of composites. HAP increases the bioactive polymer compounds without causing brittleness. In the case of PEEK/HAP contents, the correct amount of HAP is approximately 40%. Bioactive crystals and ceramic cups are other fillers needed for the HAP polymer (Oladapo *et al.*, 2019b; Park *et al.*, 2017). Dental implants made of titanium, titanium (99 NiTi), and HAP are fabricated via SLS, with combined powder HAP and NiTi throughout the SLS mechanism. It is well synthesized. Both flex sensors and “glove” have been 3D-printed, as described in Fig. 9, to establish AM technology's versatility further. LOM is also used in individual implants, consisting of layers of calcium hydroxyapatite compressed with 125 to 150 ml of glass and calcium phosphate. The size of the pores of the LOM implants depends on the size of the HAP, and it can be increased by eliminating large particles. Table 4 presents the materials used to produce various biocomposites, using different AM techniques (Oladapo *et al.*, 2020a,b,c; Florina *et al.*, 2019). Fig. 9. Represent a Flex sensor Design process and 3Dprinted sensor to undergoing mechanical stress and glove to respond to change by flexing Emerging flexible sensors based on nanomaterials of recent status and applications and Ammonia-sensing ability of differently structured hydroxyapatite blended cellulose (Lian *et al.*, 2019; Zak *et al.*, 2000).

Concluding Remarks

This study presents an AM technology study focused on a review of developing composite materials with new production technology. Various performance characteristics are presented to demonstrate the importance of AM rather than traditional production techniques. Almost the principal performance characteristics of the study of physical and mechanical properties, such as relative density, tribological properties, and the nature of the developed microstructure, were considered applicable. The composite material was reviewed for AM techniques for mechanical and bioengineering applications. The usefulness of other interdisciplinary applications such as optics, electronics, and thermal are also studied in detail. There is a need to develop AM techniques, such as searching for a new AM technique to increase the UC/SLM machine's capacity or improve the field of application. SL has great potential for the continuous production of fiber-reinforced composites. Also, additive nanocomposites and nanoparticles are presented, discussing the methods and properties of the manufacturing additives. One of AM's most effective composites is the functionally graded materials FGM analysed in this study. They offer the ability to control the composition and optimize the properties of the formed part. However, techniques for quick and accurate repeatability should be given more consideration. SLS and 3D printing can produce on-site ceramics for the compound formation and give a chance to advance the differentiated field for future research. Developing a particular post is the easiest way to make compositions using SLS and 3DP. In particular, the production of bio-composites for the manufacture of scaffolds is an area where AM has significant advantages over conventional techniques and will attract more attention in the future with its current development rate. Conclusively, opportunities, challenges, and the future direction of AM are provided as an essential step in disseminating this creative production technique in various sectors, especially in biomedical applications.

Acknowledgments

Funding: This project is funded by the Higher Education Innovation Fund (HEIF) of De Montfort University 2018–2019, UK: Research Project No.0043.06.

References

- Adeoye, A.O.M., Kayode, J.F., Oladapo, B.I., Afolabi, S.O., 2017. Experimental analysis and optimisation of synthesised magnetic nanoparticles coated with PMAMPC-MNPs for bioengineering application. *St. Petersburg. Polytech. Univ. J. Phys. Math.* 3 (4), 333–338.
- Ahn, S.H., Lee, K.T., Kim, H.J., *et al.*, 2012. Smart soft composite: An integrated 3D soft morphing structure using bend-twist coupling of anisotropic materials. *Int. J. Precis. Eng. Manuf.* 13, 631–634.
- Ain, Q.U., Khan, M., Nabavinia, M., Mujahid, M., 2017. Enhanced mechanical properties and biocompatibility of novel hydroxyapatite/TOPAS hybrid composite for bone tissue engineering applications. *Mater. Sci. Eng. C Mater. Biol. Appl.* 75, 807–815.
- Alexandre, T., Vogt, U., 2004. Layered manu. of porous ceramicpowdprecipoly. *Proc. LANE.* 497–504.
- Ashish, G., Sanjay, M.R., Srisuk, R., Parameswaranpillai, J., Siengchin, S., 2020. A comprehensive review on chemical properties and applications of biopolymers and their composites. *Int. J. Bio. Mac.* 154, 329–338.
- Balogun, V.A., Oladapo, B.I., 2019. Electrical energy demand modeling of 3D printing technology for sustainable manufacture. *Int. J. Eng.* 29 (7), 1–8.
- Bikas, H., Stavropoulos, P., Chrysosouris, G., 2016. AM meth and modeling approaches a critical review. *IJAM. Technol.* 83, 389–405.
- Castles, F., Isakov, D., 2016. Microwave dielectric BaTiO₃/ABS polymer composites. *Sci. Rep.* 6.
- Chen, Y.N., Kawazoe, Chen, G., 2018. Preparation of dexamethasone-loaded biphasic calcium phosphate nanoparticles/collagen porous composite scaffolds for bone tissue engineering. *Acta Biomater.* 67, 341–353.
- Cheung, W.L., Gibson, I., 2002. Effects of gra.poder. on the LS beh.poly. *RPJ* 8 (4), 233–242.
- Cui, L.J., Zhang, J., Zou, X., *et al.*, 2020. Electroactive composite scaffold with locally expressed osteoinductive factor for synergistic bone repair upon electrical stimulation. *Biomaterials* 230. Article 119617.
- Czyzewski, J., 2009. RP of elect. Cond. comp.3DP tech. *JMPT* 209 (12–13), 5281–5285.
- Du, X.D., Wei, L., Huang, M., Zhu, Y., Zhang, Y., 2019. 3D printing of mesoporous bioactive glass/silk fibroin composite scaffolds for bone tissue engineering. *Mater. Sci. Eng. C* 103. Article 109731.
- Exner, H., Horn, M., *et al.*, 2007. Laser micro sintering – A new method to generate metal and ceramic parts of highresolution with sub-micrometer powder. *Proc. VRAP.* 491–499.
- Feng, P., He, J., Peng, S., *et al.*, 2019. Characterizations and interfacial reinforcement mechanisms of multicomponent biopolymer based scaffold. *Mater. Sci. Eng. C Mater. Biol. Appl.* 100, 809–825.
- Feng, P., Wu, P., Gao, C., *et al.*, 2018. A multi-material scaffold with tunable properties: Towards bone tissue repair. *Adv. Sci.* 5. Article 1700817.
- Florina, D., Cojocaru, V.B., Popa, M.I., Lobiuc, A., Verestiuc, L., 2019. Biopolymers – Calcium phosphates composites with inclusions of magnetic nanoparticles for bone tissue engineering. *Int. Jou. of Bio. Macromol.* 12515, 612–620.
- Gupta, A., Ogale, A.A., 2004. Dual curing of carbon fiber reinforced photoresins for rapid prototyping. *Polym. Compos.* 23 (6), 1162–1170.
- Hon, K.K.B., Gill, T.J., 2003. Selective laser sintering of SiC/polyamide composites. *CIRP Ann. – Manuf. Technol.* 52 (1), 173–176.
- Hwang, S., Reyes, E.I., 2015. Thermo-mechanical characterisation of metal/polymer study for FDM in the 3D printing process. *J. Electron. Mater.* 44 (3), 771e7.
- Ioana, C., Frone, A.N., Brandabur, C., Panaiteanu, D.M., 2018. Recent advances in 3DP of aliphatic polyesters. *Bioengineering* 5 (1), 2.
- Isakov, D., Lei, Q., Castles, F., *et al.*, 2016. 3D-printed anisotropic dielectric composite with meta-material features. *Mater. Des.* 93, 423e30.
- Jiang, Z., Mannoor, M.S., James, T., *et al.*, 2013. 3D-printed bionic ears. *Nano Lett.* 13 (6), 2634e9.
- Kalsoom, U., 2016. A 3D printable diamond polymer composite: A novel material for fabrication. *RSC Adv.* 6 (44), 38140e7.
- Karalekas, D., 2004. Comp. RP drawback of poor mech. Prop. *JMPT* 153–154, 526–530.
- Klosterman, D.A., *et al.*, 1999. Development of a curved layer LOM process for monolithic ceramics and ceramic matrix composites. *Rapid Prototyp. J.* 5 (2), 61–71.
- Kokkinis, D., Schaffner, M., Studart, A.R., 2015. Multimaterial magnetically assisted 3D printing of composite materials. *Nat. Commun.* 6.
- Kumar, S., 2009. Manufacturing of WC–Co moulds using SLS machine. *J. Mater. Process. Technol.* 209, 3840–3848.
- Kurimoto, M., Yamashita Y., Ozaki H., Kato T., Funabashi T., Suzuki Y. 3D printing of conical insulating spacer using alumina/UV-cured-resin composite. In: *Proceedings of the IEEE. Conference on Electrical Insulation and Dielectric Phenomena (CEIDP).* 2015.
- Lian, H., Liu, X., Meng, Z., 2019. Enhanced mechanical and osteogenic differentiation performance of hydroxyapatite/zein composite for bone tissue engineering. *J. Mater. Sci.* 54, 719–729.
- Lin, Y.-H., Chiu, Y.C., Shen, Y.F., Wu, Y.-H.A., Shie, M.Y., 2018. Bioactive calcium silicate/poly-ε-caprolactone composite scaffolds 3D printed under mild conditions for bone tissue engineering. *J. Mater. Sci.* 29, 11.
- Li, S., Zahedi, S.A., Silberschmidt, V., 2017. Numerical simulation of bone cutting: Hybrid SPH-FE Approach. *Numerical Methods and Advanced Simulation in Biomechanics and Biological Processes.* 187–201. Book chapter.
- Love, L.J., Kunc, V., Rios, O., Duty, C.E., 2014. The importance of carbon fiber to polymer additive manufacturing. *J. Mater. Res.* 29 (17), 1893e8.
- Lu, L., Wong, Y.S., 2000. In situ formation of TiC composite using selective laser melting. *Mater. Res. Bull.* 1555–1561.
- Martin, J.J., Fiore, B.E., Erb, R.M., 2015. Designing bioinspired composite reinforcement architectures via 3D magnetic printing. *Nat. Commun.* 6.
- Motealleh, A., Eqtessadi, S., Pajares, A., Miranda, P., 2018. Enhancing the mechanical and in vitro performance of robocast bioglass scaffolds by polymeric coatings: Effect of polymer composition. *J. Mech. Behav. Biomed. Mater.* 84, 35–45.
- Ning, F., Cong, W., Qiu, J., Wei, J., Wang, S., 2015. AM of carbon fiber rtc using fused deposition modeling. *Compos. Part B Eng.* 80, 369e78.
- Oladapo, B.I., Adebisi Aderogba, V., Ifeoluwa Elemure, E., 2019a. Microstructural 4D printing investigation of ultra-sonication biocomposite polymer. *J. King Saud University - Eng. Sci.* 10. <https://doi.org/10.1016/j.jksues.2019.12.002>
- Oladapo, B.I., Adeoye, A.O.M., Muhammad, I., 2018b. Analytical optimisation of a nanoparticle of microstructural fused deposition of resins for additive manufacturing. *Compos. Part B Eng.* 150 (1), 248–254.
- Oladapo, B.I., Daniyan, I.A., Ikumapayi, O.M., Malachi, O.B., Malachi, I.O., 2020d. Microanalysis of hybrid characterisation of PLA/cHA polymer scaffolds for bone regeneration. *Polymer Testing* 83. Article 106341.
- Oladapo, B.I., Obisesan, O.B., Oluwole, B., *et al.*, 2020a. Mechanical characterisation of a polymeric scaffold for bone implant. *J. Mater. Sci.* 55, 9057–9069 <https://doi.org/10.1007/s10853-020-04638-y>
- Oladapo, B.I., Oshin, E.A., Olawumi, A.M., 2020e. Nanostructural computation of 4D printing carboxymethylcellulose (CMC) composite. In: Thomas, S. (Ed.), *Nano-Structures & Nano-Objects* 21. Elsevier. Article 100423.

- Oladapo, B.I., Sikiru, O.I., Mohsen, Z., Affan, K., Hazrat, U., 2020b. 3D printing and morphological characterisation of polymeric composite scaffolds. *Eng. Struct.* 216. Article 110752.
- Oladapo, B.I., Zahedi, S.A., Adeoye, A.O.M., 2019b. 3D printing of bone scaffolds with hybrid biomaterials. *Compos. Part B: Eng.* 158 (1), 428–436.
- Oladapo, B.I., Zahedi, S.A., Chong, S., Omigbodun, F.T., Malachi, I.O., 2019c. 3D Printing of surface characterisation and finite element analysis improvement of PEEK-HAP-GO in bone implant. *Int. J. Adv. Manuf. Technol.* 1–13.
- Oladapo, B.I., Zahedi, S.A., Ismail, S.O., *et al.*, 2020c. 3D printing of PEEK–cHAp scaffold for medical bone implant. *Bio-Des. Manuf.* 1–6.
- Oladapo, B.I., Zahedi, S.A., Vahidnia, F., Ikumapayi, O.M., Farooq Muhammad, U., 2018a. Three-dimensional finite element analysis of a porcelain crowned tooth. *Beni-Suef Univ. J. Basic Appl. Sci.* 7 (4), 461–464.
- Oluwale, K.B., Oladapo, B.I., Zahedi, S.A., Omigbodun, F.T., Emenuvwe, O.P., 2020. Analytical modelling of in situ layer-wise defect detection in 3D-printed parts: Additive manufacturing. *Int. J. Adv. Manuf. Technol.* 111 (7), 2311–2321.
- Park, S.-B., Lih, E., Park, K.-S., Joung, Y.K., Han, D.K., 2017. Biopolymer-based functional composites for medical applications. *Prog. Polym. Sci.* 68, 77–105.
- Perez, A.R.T., Roberson, D.A., Wicker, R.B., 2014. Fracture surface analysis of 3D-printed tensile specimens of novel ABS-based materials. *J. Fail. Anal. Prev.* 14 (3), 343e53.
- Pourhaghgouy, M., Zamanian, A., Shahrezaee, M., Masouleh, M.P., 2016. Physicochemical properties and bioactivity of freeze-cast chitosan nanocomposite scaffolds reinforced with bioactive glass. *Mater. Sci. Eng. C* 58, 180–186.
- Raz, M., Moztaazadeh, F., Kordestani, S.S., 2018. Sol-gel based fabrication and properties of mg-Zn doped bioactive glass/gelatin composite scaffold for bone tissue engineering. *Silicon* 10, 667–674.
- Rebelo, R., Fernandes, M., Figueiro, R., 2017. Biopolymers in medical implants: A brief review. *Procedia Engineering* 200, 236–243.
- Rizwan, M., Hamdi, M., Basirun, W.J., 2017. Bioglass[®] 45S5-based composites for bone tissue engineering and functional applications. *J. Biomed. Mater. Res. A* 105, 3197–3223.
- Sadeghzade, S., Emadi, R., Labbaf, S., 2017. Hardystonite-diopside nanocomposite scaffolds for bone tissue engineering applications. *Mater. Chem. Phys.* 202, 95–103.
- Saravanan, S.R., Leena, S., Selvamurugan, N., 2016. Chitosan based biocomposite scaffolds for bone tissue engineering. *Int. J. Biol. Macromol.* 93, 1354–1365.
- Selvam, S., Vasantharaj, S., Lewis Oscar, F., Selvaraj, R., Pugazhendhi, A., 2020. Natural organic and inorganic–hydroxyapatite biopolymer composite for biomedical applications. *Prog. Org. Coat.* 147. Article 105858.
- Shemelya, C.M., Rivera, A., Perez, Alexander, D., Stegeman, J., Xin, H., 2015. Mechanical, electromagnetic, and x-ray shielding characterization of a 3D printable tungstenopolycarbonate PMC for space-based applications. *J. Electron. Mater.* 44 (8), 2598e607.
- Shishkovsky, I.V., Tarasova, E., 2001. Syn. of biocomp. on the base hydroxyapatite by SLS. *Proc. LANE.* 459–464.
- Shuai, C., Yu, L., Feng, P., Gao, C., Peng, S., 2020. Interfacial reinforcement in bioceramic/biopolymer composite bone scaffold: The role of coupling agent. *Colloids Surf. B: Biointerfaces* 193. Article 111083.
- Slocombe, A., Li, L., 2001. SLS of TiC–Al₂O₃ comp. with self-prop hightemp synthesis. *JMPT* 118, 173–178.
- Srinivas, C.K., Ramesh, C.S., Channabasappa, B.H., 2009. Abrasive wear behaviour of laser sintered iron–SiC composites. *Wear* 267. <https://doi.org/10.1016/j.wear.2008.12.026>
- Sun, R.X., Lv, Y., Niu, Y.R., *et al.*, 2017. Physicochemical and biological properties of bovine-derived porous hydroxyapatite/collagen composite and its hydroxyapatite powders. *Ceram. Int* 43, 16792–16798.
- Tafaoli-Masoule, M., Shakeri, M., Zahedi, S.A., Seitz, H., Vaezi, M., 2019. 3D printing of PEEK-based medical devices. *Trans. Addit. Manuf. Meets Med.* 1 (1).
- Tofail, S.A.M., Koumoulos, E.P., Bose, A.B.S., Donoghue, L., Charitidis, C., 2018. Additive manufacturing: Scientific and technological challenges, market uptake and opportunities. *Mater. Today* 21, 22–37.
- Umme, K., Nesterenko, P.N., Paull, B., 2016. Recent developments in 3D printable composite materials. *RSC Adv.* 6, 60355.
- Vaucher S., Andre C., Parascivescu D., Beffort O., 2002 SLS of alum. sili carbmetalmatrix comp. *Mater Week.*
- Yu, P., Schaffer, G.B., 2009. Micro. Evol. preeless infi.alum.alloy parts fab. by SLS. *Acta Mater.* 57, 163–170.
- Zahedi, S.A., Demiral, M., Roy, A., Silberschmidt, V.V., 2013. FE/SPH modelling of orthogonal micro-machining of fcc single crystal. *Comput. Mater. Sci* 78, 104–109.
- Zahedi, S.A., Kodsí, C., Berto, F., 2019. Numerical predictions of U-notched sample failure based on a discrete energy argument. *Theor. Appl. Fract. Mech* 100, 298–306.
- Zak, G., Park, C.B., Haberer, M., Benhabib, B., 2000. Mechanical properties of short-fibre layered composites: Prediction and experiment. *Rapid Prototyp. J.* 6 (2), 107–118.
- Zhan, Y., 2001. RP and combsynth TiC/Ni funct gradient. *Mater. Sci. Eng. A* 299, 218–224.
- Zhong, W., Li, F., Zhang, Z., Song, L., Li, Z., 2001. Short fiber reinforced composites for fused deposition modeling. *Mater. Sci. Eng. A* 301 (2), 125e30.

Marine Polysaccharide-Based Composite Hydrogels

Saad Salman, Syed H Khalid, Ikram U Khan, and Sajid Asghar, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Fahad H Shah, University of Peshawar, Peshawar, Pakistan

Muniba Tariq, The University of Lahore, Islamabad Campus, Islamabad, Pakistan

© 2021 Elsevier Inc. All rights reserved.

Introduction

Hydrogel, a class of DDs, are classified as 'intelligent' drug-delivery responsive to pH, temperature and other physiological, and biochemical factors (Mahinroosta *et al.*, 2018; Mo *et al.*, 2020). These gels are comprised of vast polymeric networks to absorb large amounts of water without being dissolved. Composite hydrogels of marine polysaccharide (MP) origin, such as ulvan (Tziveleka *et al.*, 2019), gelatin (Rodríguez-Rodríguez *et al.*, 2020), alginate (Fernando *et al.*, 2020), chitin (Shen *et al.*, 2016), carrageenan (Yegappan *et al.*, 2018), fucoidan (Fitton *et al.*, 2019), agarose (Zarrintaj *et al.*, 2018), chitosan (Rodríguez-Rodríguez *et al.*, 2020), and chitooligosaccharides (Park *et al.*, 2018) are well studied. Natural polymers that are vulnerable to enzymatic degradation, or synthetic-polymers, having hydrolysable moieties, have been used to make hydrogels. Out of all the hydrogels, marine polysaccharides obtained from natural sources are of prime importance due to their low toxicity, degradability, and biocompatibility (Cardoso *et al.*, 2016; Kuznetsova *et al.*, 2020; Laurienzo, 2010; Lee *et al.*, 2017).

The discovery of a variety of active compounds was thought to be potential candidates for therapeutic purposes but only a few are successful. Low 'bioavailability' and the rate at which a drug reaches the target tissue are the two main factors leading to the poor activity of the therapeutic compounds (Li *et al.*, 2019; Stuurman *et al.*, 2013). The decrease in bioavailability can lead to decreased plasma concentration of drugs hence, requiring re-administration. This increases the chances of overdose. The controlled drug delivery systems (DDs) are used as an alternative for the regulation of bioavailability of the therapeutic agents (Li *et al.*, 2019). In such systems, the drug is allowed to release in a controlled fashion by incorporating the active therapeutic-agent into the polymeric matrix. The time for drug release may vary from hours to months or years. Drug carriers have been studied as natural or synthetic polymers containing hydrophobic and hydrophilic components. But DDs come with the price of certain limitations like manufacturing costs, time constraints, and toxic byproducts. To make 'intelligent DDs', researchers have strived to regulate the functionality, biodegradability and environmental response of the DDs by studying their physical as well as chemical characteristics (Talebian and Foroughi, 2020; Zhang *et al.*, 2020a). Other traits like electrostatic charges, ionic interactions, and multiple functional groups have made marine polysaccharide quite a significant polymer in delivering genes, metals, peptides, proteins, antigens, and drugs. The preparation, physicochemical properties, and applications will be briefly discussed. And various classes of MP-hydrogel composites will be further described in the article.

Marine Polysaccharide Hydrogel Composites

Polymeric networks containing a large number of hydrophilic groups are cross-linked with each other to form hydrogels. Due to the presence of physical and/or chemical bonds between the polymeric chains, they do not dissolve in the water despite having a high affinity for it. The soft and rubbery texture of the fully-swollen hydrogels resembles with living tissues. It reduces irritation to the surrounding tissues, and in between the body fluids and hydrogel surface, minimizes protein adsorption, and cell adhesion (Palmese *et al.*, 2019). And the chances of the negative immune reactions are also reduced. Hydrogels make excellent drug delivery vehicles owing to some of their unique characteristics (Fu, 2019). Muco- and bioadhesive characteristics of these hydrogel composites enhance tissue permeability and drug residence is found in many polymers, for example, PAA, PEG, PVA (Chopra *et al.*, 2020; Hanafy *et al.*, 2019). Due to the inter-chain bridges and mucous glycoproteins, they demonstrate adhesive-property.

Chitosan is unique from other marine polysaccharides due to the presence of nitrogen in its molecular structure and capacity to form polyelectrolyte-complexes (Islam *et al.*, 2017). It does not encourage an immune response (Foster *et al.*, 2015). As chitosan is biodegradable, non-toxic, and can also be sterilized, these properties make it a great excipient, perfect for the release of therapeutic agents in a controlled way. They are extremely versatile materials with a wide range of applications in the biotechnological and biomedical fields. Ahsan *et al.* developed a chitosan-based composite hydrogel cross-linked with glutaraldehyde and loaded with I-131 and tested in a breast cancer xenograft mouse model (Ahsan *et al.*, 2020). The result showed a decrease in the tumor progression rate and prevented more than half of the tumor recurrence and metastatic spread.

Carrageenan (car-) are comprised of linear sulfated polysaccharides isolated from the species of Rhodophyta (Patel, 2012; Shukla *et al.*, 2016). These polysaccharides and their derivatives have been exploited in cosmetics, foods, and pharmaceuticals. Car- are exploited in the drug delivery system as a controlled release agent that possesses antioxidant properties as well (Genicot *et al.*, 2018; Li *et al.*, 2014). There are three variants of car- i.e., lambda, kappa, and iota, that possess a range of properties such as biocompatibility, biodegradability, mechanical strength, hydrophilicity, and stability (Derkach *et al.*, 2018; Ghanbarzadeh *et al.*, 2018; Sahiner *et al.*, 2017). Car- composite films in combination with glycerol and citric acid further ameliorate the anti-microbial activity (Khare *et al.*, 2016; Sedayu *et al.*, 2019).

Covalent Interactions of MP-Based Hydrogel Composites With Drug/Metal

Owing to the porous structure of the hydrogels, the metals/drug, through physical mixing, is removed from the hydrogel. The rate of the chemical and enzymatic-cleavage of the polymer-drug bond is controlled by covalently bonding the drug to the hydrogel-matrix (Li and Mooney, 2016). This covalent interaction may result in delaying the release of drug from a few weeks to months. The sustained release of paclitaxel was observed by the help of a thermosensitive-polyphosphazene-paclitaxel conjugate gel (Chun *et al.*, 2009). Osteogenic differentiation of human mesenchymal stem cells was facilitated with the conjugation of dexamethasone to the photo-reactive mono-acylated PEG (Briggs *et al.*, 2009). The daunomycin cross-linked to poly-(aldehyde guluronate) (Bouhadir *et al.*, 2000) was released based on the hydrolysis-rate of the drug-polymer covalent-linkage ranging from two days to six weeks.

There are two easy ways to do the drug/metal loading of the hydrogels, one way is the cross-linking diffusion of the active agent into the hydrogel pores and the other is how in the presence of a drug, macromolecule, or proteins cross-linking of the polymeric chains is done (Akhtar *et al.*, 2016). The initial hydrogel swelling resulted in bursting and a typical drug-release of 70% occurred but by the use of cross-linker, the loss was reduced to about 10%–25% (Zhang *et al.*, 2020b).

Micro-/Nanocapsules and Interpenetration Networks

The drug-containing micro- and nanocapsules can be incorporated into the hydrogels. For example, the encapsulation of TGF-beta1 loaded gelatin-microparticles within the biodegradable polymer oligo-(polyethylene glycol fumarate) gel can help control the release of the TGF-beta1 over the period of one month (Holland *et al.*, 2003). The drug-release of dexamethasone with Chitosan hydrogel composite was slowed down by approximately 6% versus PVA-based hydrogels encapsulated-with steroid loaded microspheres (Long *et al.*, 2019). Researchers have now dispersed microparticles containing drugs in the hydrogel-matrix without affecting the swelling as well as the hydrogel network. As the hydrogel continues to degrade, the drugs and proteins that have been encapsulated are released and then they diffuse to the outside medium.

The strength of polymers can be increased by interlacing two or more polymeric chains together. The cross-linked MP-network expands into monomers of the polymer. These monomeric subunits are polymerized and form a physically intertwined network called an interpenetrating network. They are arranged in such a way that one polymer remains at rest state while the other runs through it in a cross manner, e.g., semi-IPN polyether, silk, PVP, etc.

Hydrophobic Interactions of Hydrogels

One class of hydrogel-systems is the thermo-reversible hydrogels, which have been engineered by researchers, function (by depending on environmental temperature) in the formation of transient gel or liquid states. Flowable liquid-solution is used for junction production between chains by yielding semi-rigid gel due to the property of such polymers that use hydrophobic-interactions or secondary bonding to their advantage. When the temperature of the system goes beyond the lower critical solution temperature (LCST) then the material converts from hydrophilic to hydrophobic (Klouda and Mikos, 2008). Polymer solution has importance in biomedical applications due to its property of having decreased viscosity plus forming gel above a LCST. These are injected in the body as a liquid that forms gel when the body temperature exceeds LCST. This acts as transporter matrices for a broad variety of biomedical as well as the pharmaceutical applications (Mahinroosta *et al.*, 2018; Mo *et al.*, 2020). Invasive surgeries are not required and delivery of agents to a defected-site without significant negative-effects for introducing these injectable, gelling systems. Negative effects may be the use of organic-solvents or the formation of toxic-byproducts. Custom produced scaffold designs have been eliminated by the use of injectable hydrogels.

The collection of co-polymers is based on chitosan hydrogels which in solution demonstrates gelation neutralized with polyol salts (Liu *et al.*, 2016). This method is used for the mixture of glycerol-phosphate-disodium salt (GP) and chitosan that is sensitive to temperature. At 37°C room temperature, the gel-mixture remains a clear liquid.

An injectable thermoreversible gel was developed by a few scientists (Bhattarai *et al.*, 2010) that utilized chitosan for gelation. Chitosan PEG co-polymers (made by Schiff base and sodium cyanoborohydride by chemically-grafting monohydroxy-PEG on the backbone of chitosan) were used for the preparation of gel. By balancing the ratio of hydrophilic and hydrophobic-groups the co-polymer goes from the injectable-solution at room-temperature to the gel at body temperature via a thermo-reversible route. The passage of the gel solution is temperature-dependent. At approximately 25°C there is an increase in viscosity of hydrogel. Below the temperature at which transition occurs, injection of the solution with a needle of 22 G can be done. This is further created into a transparent gel by the complete transformation. This occurs above the transition temperature. High temperature promotes hydrophobic interactions between polymer chains, while at low-temperature H-bonding takes place between PEG molecules, hence resulting in the creation of gel (Hu *et al.*, 2019; Ranganathan *et al.*, 2018). Some other derivatives of cellulose with hydrophilic moieties also possess such thermo-sensitive gelation (Kabir *et al.*, 2018).

Many other hydrogels have been prepared and formulated with the use of co-polymers combined with poly(N-isopropyl acrylamide) (PNIPAM) as well as poloxamers which have dominant hydrophobic-interactions at high temperatures (Burdukova *et al.*, 2010). In reversible hydrogel formations, such polymers make appropriate candidates. Precipitation of PNIPAM solutions takes place above the 32°C. H-bonding between the polymer and polar-molecules results in the polymer-dissolution at low

temperatures. Dehydration of hydrophobic isopropyl groups leads to the creation of gel at a higher temperature. This process takes place at some stage in the coil-to-globule transition. For the regulation in temperature of gelation closer to physiological temperatures in order to improve the mechanical-strength and advance the bio-compatibility of the hydrogel, PNIPAM has been adapted with many natural polymers (Lanzalaco and Armelin, 2017). Deliverance of peptides, drugs, cells, and proteins rapidly in the body (by injection) can take place by the use of these formulations when these agents are integrated or mixed with the dissolved polymer. The controlled release system is provided by the gel which is formed in the process. Polymers like poloxamers, triblock copolymers as well as PEO-PPO-PEO develop hydrogel when the concentration of the polymers is retained beyond a critical value, and the temperature is above the polymeric-LCST (Klouda and Mikos, 2008). These polymers also have a central hydrophobic-segment which is joined with two regions that are hydrophilic in nature. Chitosan-poloxamer solution was verified as an injectable delivery vehicle due to its solution-gel transition which was $\sim 25^{\circ}\text{C}$ (Varshosaz *et al.*, 2008).

Physical Association Networks

Two conditions must be satisfied by the MP-polymeric network to satisfy requisite hydrogel composite features. Firstly, strong inter-chain interactions are required for the development of semi-permanent junctions in the molecular-network. Secondly, in the polymer network, the water molecules should have access and residence, promoted by the network. Non-covalent strategies are utilized to prepare the gels that meet all the above-mentioned demands and they capitalize on hydrophobic; H-bonding and electrostatic forces present in between the chains of polymers (Fu *et al.*, 2018; Picchioni and Muljana, 2018). Ionic, poly-electrolyte, inter-polymer complex, and hydrophobic-associations (major physicals interactions) are present in these MP gels. The formation of gel can also be reversed as these are pure physical interactions. Also, tunable gel swelling behavior can be achieved if the nature and concentration of the second component of the fabrication process are adjusted. Chitosan-based physical-gels have a short life span of some days to almost about a month in physiological media; by mixing various components under appropriate conditions, these can be prepared. As a result, for short-term drug-release applications, physical gels make a good source. Gelatin does not require any toxic covalent-linker-molecules (Jătaru *et al.*, 2013), so it is safe for a clinical application as it is but it has poor mechanical strength and uncontrolled dissolution due to which they have limited applications (Ahmadi *et al.*, 2015).

Physical Mixtures and Secondary Bonding

Polymer-blends between MP and other water-soluble nonionic-polymers can also result in the formation of hydrogels. These polymer mixtures form inter-polymer complexations or crystal-junction points due to lyophilization and a freeze-thaw process (Parhi, 2017). The cross-linking sites of hydrogels are formed due to this interaction between the chains. In the case of PVA-polymer, when the negativity of chitosan is increased, the formation of PVA crystallites is affected. Hence, less ordered structures of hydrogels are developed. A composite of chitosan and polyethyleneimine (PEI) (Lu *et al.*, 2014) is widely used as a gene transfection agent. 3D hydrogel was produced within five minutes when PEI was mixed with alginate-hyaluronic for tissue repairing (Rajaram *et al.*, 2015).

Chitosan-chitosan self-associations take part in holding the gel structure together. At pH 7.5, chitosan is insoluble and crystallite formation occurs because of this between its chains. Chitosan alone can also be used for hydrogel formation, without the need to add any other polymer or complexing-molecule, as shown by Ladet *et al.* (2008) by the process called as hydro-alcohol gel creation. Sodium hydroxide solution could be used to neutralize the amino-group of chitosan and the process of gel creation depended on it. H-bonds, hydrophobic-interactions, and chitosan-crystallites were formed by prohibiting ionic-repulsion between the polymer chains. Observations included hydrogels macroscopic shrinkage during gel depletion and neutralization. Multi-layered onion-like hydrogels were prepared with the gelatin (Ladet *et al.*, 2011). This gelation method was not constant which could help in the encapsulation of drugs and their delivery.

Ionic Complexes

The chitosan can interact with the molecules that are anionic in nature while car- can interact with cationic molecules. Between small negatively charged molecules and chitosan, ionic-complexes of mixed charged systems can be prepared (Ahmadi *et al.*, 2015; Moura *et al.*, 2011) or between the negatively charged metals like Pt (II), Pd (II), and Mo (VI) (Nie *et al.*, 2016). The charge density of the negatively-charged agents and their size determines the hydrogels owning a variety of material-characteristics that can be obtained upon these ionic-interactions. The concentration of chitosan-polymer and degree of de-acetylation also determines the same. Chitosan is bound through its protonated amino-groups and this is done by small molecules as well as anions. While, on the other side, instead of the electrostatic-interaction, the metal-ions form a coordinate covalent bond with the polymer (Ahmadi *et al.*, 2015; Nie *et al.*, 2016). The bonds found in anionic-molecules and the polycation are weaker than this strong bonds. The global charge-density of small molecules is affected due to environmental pH and pKa. Whereas, the charge density of metal anions is independent of pH. There is very little or no charge at all above the pH 6 in chitosan; it has a pKa ~ 6.3 , so its use is reduced under physiological conditions. To attain strong ionic interactions, high charge density must be present between the anionic molecules; their MW should also be very small so that they can easily diffuse through the polymer matrix for the quick and faster formation of electrostatic bonds. Other secondary interchain interactions also contribute to ionic complexation. The

H-bonding present between the ionic-molecules and the hydroxyl-groups of chitosan could be one of the interactions or it could be the interaction between the post-cationic charge neutralization interaction between the de-acylated chitosan chains (Foster *et al.*, 2015; Islam *et al.*, 2017). Such interactions take part in modulating to state distinctive material properties, like pH sensitivity and enhancing the physical properties of hydrogels.

The brittleness and the rigidity of the κ -gels could be reduced by blending it with either λ - or ι - (BeMiller, 2019). κ - works opposite to ι - in terms of reactivities to K^+ and Ca^{2+} salts. ι - can form a relatively stronger and stable gel as compared to κ - with Ca^{2+} salts, which do not bleed (syneresis), soft and resilient. The gel is thawed and frozen without damaging the texture. The syneresis could be prevented by blending λ - with κ - (Zia *et al.*, 2017). The ι - demonstrates thixotropic behavior in aqueous solutions while κ - does the same in milk. The gel of κ - is weak but fine particles of a material can be suspended e.g., chocolate milk and cocoa. The gels of the car- are thermo-reversible in the range of 40–70°C depending upon the presence of cations and concentration. ι - gels are lucid while the κ - gels are cloudy. But the hard gel is better for flavor release making κ - the superior in this regard (Loret *et al.*, 2009; Zia *et al.*, 2017). The acidic pH tolerability and stability of κ - is poor and in the range of 4–10 but by adding other car- it may help in building the pH tolerance. The solubility of λ - is more in cold 50% sugar solutions as compared to ι - (insoluble) and κ - (soluble only in hot solution). The λ - addition in syrups is preferable (Loret *et al.*, 2009). λ - and ι - are soluble in 10% salt solutions whereas κ - is insoluble. Freeze-thaw stability is absent in κ - but present in ι - and λ -. The gel texture could be improved by the addition of ι - (BeMiller, 2019). κ - forms brittle and stiff gels whereas ι - forms elastic and soft gels, so by combining these two gels the overall texture could be improved (Zia *et al.*, 2017). At 20°C, all salts are soluble in λ -, but $[Na^+ \text{ salt}]$ is only soluble for ι - and/or λ -. In cold milk, the ι - and κ - are insoluble but λ - thickens it. κ -, ι -, λ - individually can play wonder in the food and pharmaceutical industries but their blends give them a set of overtly improved unique characteristics (Ghanbarzadeh *et al.*, 2018). By pairing ι - and κ -, the gelatin alternative could be achieved. There is a synergy with starch of ι - and absence of κ - and λ - with locust bean gum but absence in case of λ - and ι - (Tang *et al.*, 2021). Shear reversibility is not present in κ - but do present in λ -, and ι - (Torres *et al.*, 2017; van de Velde *et al.*, 2005). The "melt-in-your-mouth" the sensation is given by ι - unlike κ - that gives hard and brittle to soft and brittle textures depending upon the concentration. κ - with λ - are used for bodying in syrups. κ - and ι - are used as an alternative to gelatin (BeMiller, 2019; Blakemore, 2016). κ - and λ - could be used in the preparation of suspensions. λ - and κ - could be used for emulsion stabilization. λ - do not need any ions whereas κ - and ι - need K^+ and Ca^{2+} to form a viscous solution whereas λ - do not need any ions (Blakemore, 2016). ι - and κ - are used for mouthfeel and texture. Fat stabilization can be achieved with the help of ι - and λ -. All three car- can use as a binder, emollient, and to prepare suspension/dispersion. The difference in properties of the car- depends upon the position and number of ester sulfate groups. The more the ester sulfate groups present in the car-, the lower the temperature of solubility. It also contributes to gel inhibition in λ - while lower gel strength in ι - and κ - (BeMiller, 2019). But by the addition of cations, the dispersion increases consequently increasing the temperature of gelling, re-melt, and dissolution of car- (Blakemore, 2016).

Polyelectrolyte Complexes (PECs)

Polyelectrolytes do develop electrostatic-interactions with marine polysaccharides although the ionic-molecules present in the ionic-complexation are very different from the polyelectrolytes (Ahmadi *et al.*, 2015). The polyelectrolyte-chitosan interaction is much stronger than the other types of interactions like the van der Waals as well as H-bonding. These complexes have great advantages. No catalysts, reactive agents, or organic precursors are used for their complexation. PECs have a simple and reversible complexation as they only contain chitosan and polyelectrolyte. Chitosan-based PEC networks are prepared with the use of negatively-charged water-soluble macromolecules (Jana *et al.*, 2014), the negatively-charged synthetic-polymers, and proteins (Peniche *et al.*, 2018). The stability of the compounds is determined by the strength of the ion, the density of the charge, solvent, temperature, and pH (Ahmed, 2015; Lin and Anseth, 2009; Peniche *et al.*, 2018). Ionic-interactions as well as the PEC hydrogel-properties are regulated by the pH of the environment.

The uses of the car- are also underpinned by their metal-binding capabilities. The 3, 6-anhydro-bridge and degree of sulfation cause the three car- to selectively bind with various metal ions and demonstrated different rheological properties (Cao *et al.*, 2018). κ - having one negatively charged sulfate group prefer monovalent cations and selectively binds to Cs^+ , Rb^+ , and K^+ but not with Na^+ . ι - binds selectively with Ca^{2+} due to the presence of two sulfate groups (Covis *et al.*, 2016). λ - (three sulfate groups) do not bind with Cr^{3+} but bind with Al^{3+} and Fe^{3+} (Running *et al.*, 2012). This is because of the different properties of metal ions, different ionic hydration, and electrostatic interactions with the car- (Salman *et al.*, 2020). These monovalent and divalent ions reduce the repulsion of κ - and ι - helices resulting in stabilization. λ - do not form helical structure due to the 4C_1 conformation and absence of 3, 6-anhydro-bridge ring thus does not form gel. The metal-binding properties of the pure car- were reported in a study for divalent and trivalent metal ions (Khotimchenko *et al.*, 2010) while we reported the blends of κ - with ion-exchange resins for Cu^{2+} sorption (Salman *et al.*, 2020).

Cross-Linked Networks

Even without the addition of cross-linkers, the physically-bounded hydrogels are capable of gel-formation, yet there seem to be certain drawbacks. As it can lead to inconsistent performance in vivo due to difficulty in controlling the functioning of chemicals, pore sizes, and degradation of physical gel. Permanent hydrogel networks are directly produced by *chemically cross-linking* through

linking covalent-bond between the polymer-chains. For the production of chitosan $-NH_2$ and $-OH$ chemical-handles as well as cross-linker, are utilized. This also includes the formation of different numbers of other linkage chemistries. The other methods of network formation include small molecule cross-linker, polymer-polymer reaction, or enzyme-catalyzed reactions.

He *et al.* developed the light or photo-sensitive chitosan hydrogel within situ with the help of functionalizing the polymer with an acid group ($-N_3$) $[COO]$ (He *et al.*, 2017). Gelation is caused when the azide group is exposed to sunlight; it is changed into a nitrene group. The thermo-sensitive, chitosan-pluronic hydrogels are developed and are cross-linked by UV sunlight (Park *et al.*, 2009).

Enzymatic cross-linking is an extra-ordinary technique use in biomedical applications and in-situ hydrogel formation. Horseradish peroxidase (HRP) B-type hemoprotein composed of a single chain which is used to catalyze reactions associated with cross-linking. Jin *et al* used the chitosan derivatives that were water-soluble such as glycolic acid to produce chitosan-based with HRP and H_2O_2 that were injectables (Jin *et al.*, 2009). In gelation, varying the polymer concentration, water contents of gel, enzymatic degradation, and mechanical properties can be modified according to requirement, and also gelation time can be varied by polymer concentration. Enzymes, Tyrosinase, involves in the hydrogel in situ as it is an oxidizing agent used in gelation. Tyrosinase oxidizes the tyrosyl to quinone which forms intermolecular linkage (Jin *et al.*, 2014).

Drug Loading and Release

The hydrogel composites for DDs depend on the physical and chemical properties of the gel. And the choice of hydrogel materials network arrangement and drug loading method must be made to complement the properties of the drug (i.e., hydrophobicity, charge) and its mode of action (sustained drug release versus rapid, high exposure). Three major drug loading approaches are (1) Diffusion, (2) Entrapment, and (3) Interaction. Each method has advantages and disadvantages and should be chosen after careful observation of the hydrogel network used and the nature of the drug. The drug release from a hydrogel can occur in one of three different modes. (1) Diffusion, (2) Chemical/environmental stimulation, and (3) Enzyme specific stimulation.

Chitosan shows the pH-sensitive behavior of weak polybasic nature dissolving easily at low pH. To take advantage of this phenomenon, PEC hydrogels dissolved in the stomach have been prepared to change the charge balance inside the hydrogel causing swelling of PEC complexes (Ahmadi *et al.*, 2015). The swelling of hydrogels in the stomach is limited but triggered in the intestine due to further changes in pH. In one example, ionically cross-linked succinyl-chitosan (suc-chi)/alginate hydrogels showed release of as little as 11.6% of nifedipine at pH 1.5 and as much as 76% at pH 7.4 after 15 h (Dai *et al.*, 2008). This particular polyelectrolyte complex was made sensitive to higher pH due to a large number of carboxylated groups in the network. This conclusion suggested that the suc-chi/alginate hydrogel bead could be a potential polymer carrier in the intestinal area for drug delivery. Berger *et al.* had observed several different PEC systems based on chitosan (Berger *et al.*, 2004). pH-sensitive chitosan-acrylamide-grafted hydroxyethyl cellulose (AAM-g-HEC)-based semi-IPN hydrogel microspheres were prepared for the release of pH-sensitive drugs, i.e., slower release at pH 1.2 and faster at 7.4, explaining their potential drug release application in the GIT tract (Ahmed *et al.*, 2009). If the hydrogel expresses thermo-responsive behavior then the drug release form such as IPN is further affected by temperature (e.g., PNIPAM-chitosan) (Burdukova *et al.*, 2010). In addition to PEC and IPN networks, polyblend-based hydrogels also exhibit pH sensitivity. If the mixing part is neutral and hydrophilic (polarized and capable of H-bonding), such as PEO and polyvinylpyrrolidone (PVP) under acidic conditions, chitosan's primary amine is protonated, causing repulsion in the chain and subsequent swelling or breaking up (Patel and Amiji, 1996).

By incorporating the magnetic particles into the cross-linked MP hydrogel, a typical magnetic field sensitivity can be achieved. So, a chitosan-based nanocomposite hydrogel composed of chitosan and montmorillonite, a nanohydrogel exhibiting an exfoliated nanostructure under electro-stimulation was reported (Haerudin *et al.*, 2010). The main mechanisms of drug release from the electro-responsive hydrogels include drug solution ejection during deswelling, diffusion, changed drug electrophoresis, and electro-induced gel erosion.

Car- blends for the Tolterodine L-Tartrate controlled release by simple physical mixing. They reported that the carrier behavior changes with different combinations of car-. Also, the release rate was slower for the pure car- but by incorporating λ - along with other car-, controlled release formulations were obtained (Nanaki *et al.*, 2010). While the water barrier, mechanical (Rhim and Wang, 2013), and electrolytic properties were obtained through the preparation of ternary biohydrogel blends of agar/ κ -car-/konjac glucomannan and kappa/cellulose derivatives (Dafe *et al.*, 2017). In another study, λ - and ι - blends were effective matrices for sustained release formulation of fluvastatin. Higher dissolution profiles were obtained for physical mixtures of car- and drug as compared to their corresponding complexes (Karavas *et al.*, 2014). The biodegradable film with an antioxidant barrier, and pH-responsive properties was obtained by blending *Prunus maackii* extract with κ -car-/hydroxypropyl methylcellulose. κ - was blended with carboxymethyl cellulose for the effective delivery of *Lactobacillus plantarum* (Dafe *et al.*, 2017). The car-/alginate based hydrogels were reported recently for the lidocaine controlled release (Rasool *et al.*, 2020).

Conclusions

Due to the ease of fabrication, gelation, and chemical structure, the MP based hydrogels are quite attractive biomaterials. These gels may have tailor-made porosities, mechanical strengths, and dimensions that can be developed to support their area of application.

Notably, in this article, we saw how the distinct ionic characteristics of car- and chitosan can offer even wide latitude to biomaterial engineers in the types of hydrogel composites that can be developed, and the processes by which they fragment and deteriorate in the body. In "smart" delivery systems the flexibility of these MP as a major component is compounded by its biocompatibility and in-vivo biodegradability. MP has received significant attention in the development of injectable, in-situ gelling systems for tumor treatment, tissue regeneration and as a delivery vehicle in oral and ophthalmic systems. We consider these current advances will produce delivery systems of the next generation as we gain a greater understanding of the dynamics of mixed MP-chain networks. We will be capable of adapting these materials for different metals and drug formulations, release conditions. Cheap, non-toxic, environment friendly and efficient MP-hydrogel composite systems can move closer to clinical availability once these design parameters have been set.

References

- Ahmadi, F., Oveis, Z., Samani, S.M., Amoozgar, Z., 2015. Chitosan based hydrogels: Characteristics and pharmaceutical applications. *Research in Pharmaceutical Sciences* 10, 1–16.
- Ahmed, A., Naik, H., Sherigara, B., 2009. Synthesis and characterization of chitosan-based pH-sensitive semi-interpenetrating network microspheres for controlled release of diclofenac sodium. *Carbohydrate Research* 344, 699–706.
- Ahmed, E.M., 2015. Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research* 6, 105–121.
- Ahsan, A., Farooq, M.A., Parveen, A., 2020. Thermosensitive chitosan-based injectable hydrogel as an efficient anticancer drug carrier. *ACS Omega* 5, 20450–20460.
- Akhtar, M.F., Hanif, M., Ranjha, N.M., 2016. Methods of synthesis of hydrogels. A review. *Saudi Pharmaceutical Journal* 24, 554–559.
- BeMiller, J.N., 2019. Chapter 13 - Carrageenans. In: BeMiller, J.N. (Ed.), *Carbohydrate Chemistry for Food Scientists*, third ed. AACC International Press, pp. 279–291.
- Berger, J., Reist, M., Mayer, J.M., *et al.*, 2004. Structure and interactions in covalently and ionically crosslinked chitosan hydrogels for biomedical applications. *European Journal of Pharmaceutics and Biopharmaceutics* 57, 19–34.
- Bhattacharj, N., Gunn, J., Zhang, M., 2010. Chitosan-Based Hydrogels for Controlled, Localized Drug Delivery. *Advanced Drug Delivery Reviews* 9, 83–99.
- Blakemore, W.R., 2016. Polysaccharide ingredients: Carrageenan. In: *Reference Module in Food Science*. Elsevier.
- Bouhadir, K.H., Kruger, G.M., Lee, K.Y., Mooney, D.J., 2000. Sustained and controlled release of daunomycin from cross-linked poly (aldehyde guluronate) hydrogels. *Journal of pharmaceutical sciences* 89, 910–919.
- Briggs, T., Treiser, M.D., Holmes, P.F., *et al.*, 2009. Osteogenic differentiation of human mesenchymal stem cells on poly(ethylene glycol)-variant biomaterials. *Journal of Biomedical Materials Research. Part A* 91, 975–984.
- Burdukova, E., Li, H., Ishida, N., O'Shea, J.-P., Franks, G.V., 2010. Temperature controlled surface hydrophobicity and interaction forces induced by poly (N-isopropylacrylamide). *Journal of Colloid and Interface Science* 342, 586–592.
- Cao, Y., Li, S., Fang, Y., *et al.*, 2018. Specific binding of trivalent metal ions to λ -carrageenan. *International Journal of Biological Macromolecules* 109, 350–356.
- Cardoso, M.J., Costa, R.R., Mano, J.F., 2016. Marine origin polysaccharides in drug delivery systems. *Marine Drugs* 14.
- Chopra, H., Kumar, S., Singh, I., 2020. Bioadhesive hydrogels and their applications. In *Bioadhesives in Drug Delivery*. Wiley Online Books.
- Chun, C., Lee, S.M., Kim, S.Y., Yang, H.K., Song, S.-C., 2009. Thermosensitive poly (organophosphazene)-paclitaxel conjugate gels for antitumor applications. *Biomaterials* 30, 2349–2360.
- Covis, R., Guegan, J.-P., Jętić, J., *et al.*, 2016. Structural and rheological properties of kappa (κ)-carrageenans covalently modified with cationic moieties. *Journal of Polymer Research* 23, 78.
- Dafe, A., Etemadi, H., Zarredar, H., Mahdavinia, G.R., 2017. Development of novel carboxymethyl cellulose/k-carrageenan blends as an enteric delivery vehicle for probiotic bacteria. *International Journal of Biological Macromolecules* 97, 299–307.
- Dai, Y.-N., Li, P., Wang, A., Wei, Q., 2008. A novel pH sensitive N-succinyl chitosan/alginate hydrogel bead for nifedipine delivery. *Biopharmaceutics & Drug Disposition* 29, 173–184.
- Derkach, S.R., Voron'ko, N.G., Kuchina, Y.A., *et al.*, 2018. Molecular structure and properties of κ -carrageenan-gelatin gels. *Carbohydrate Polymers* 197, 66–74.
- Fernando, I.P.S., Lee, W., Han, E.J., Ahn, G., 2020. Alginate-based nanomaterials: Fabrication techniques, properties, and applications. *Chemical Engineering Journal* 391, 123823.
- Fittin, J.H., Stringer, D.N., Park, A.Y., Karpinić, S.S., 2019. Therapies from fucoidan: New developments. *Marine Drugs* 17.
- Foster, L.J.R., Ho, S., Hook, J., Basuki, M., Marçal, H., 2015. Chitosan as a biomaterial: Influence of degree of deacetylation on its physicochemical, material and biological properties. *PLoS One* 10, e0135153.
- Fu, J., 2019. Hydrogel properties and applications. *Journal of Materials Chemistry B* 7, 1523–1525.
- Fu, J., Yang, F., Guo, Z., 2018. The chitosan hydrogels: From structure to function. *New Journal of Chemistry* 42, 17162–17180.
- Genicot, S., Préchoux, A., Correc, G., *et al.*, 2018. Carrageenans: New Tools for New Applications. In *Blue Biotechnology*. Wiley Online Books.
- Ghanbarzadeh, M., Golmoradizadeh, A., Homaei, A., 2018. Carrageenans and carrageenases: Versatile polysaccharides and promising marine enzymes. *Phytochemistry Reviews* 17, 535–571.
- Haerudin, H., Pramono, A., Kusuma, D.S., *et al.*, 2010. Preparation and characterisation of chitosan/montmorillonite (MMT) nanocomposite systems. *International Journal of Technology* 1, 65–73.
- Hanafi, H.A.N., Leporatti, S., El-Kemary, M.A., 2019. Mucoadhesive hydrogel nanoparticles as smart biomedical drug delivery system. *Applied Sciences* 9.
- He, M., Han, B., Jiang, Z., *et al.*, 2017. Synthesis of a chitosan-based photo-sensitive hydrogel and its biocompatibility and biodegradability. *Carbohydrate Polymers* 166, 228–235.
- Holland, T.A., Tabata, Y., Mikos, A.G., 2003. In vitro release of transforming growth factor- β 1 from gelatin microparticles encapsulated in biodegradable, injectable oligo (poly (ethylene glycol) fumarate) hydrogels. *Journal of Controlled Release* 91, 299–313.
- Hu, W., Wang, Z., Xiao, Y., Zhang, S., Wang, J., 2019. Advances in crosslinking strategies of biomedical hydrogels. *Biomaterials Science* 7, 843–855.
- Islam, S., Bhuiyan, M.A.R., Islam, M.N., 2017. Chitin and chitosan: Structure, properties and applications in biomedical engineering. *Journal of Polymers and the Environment* 25, 854–866.
- Jana, S., Banerjee, A., Gandhi, A., 2014. Preparation and characterization of chitosan based polyelectrolyte complex as a carrier of aceclofenac. *Journal of PharmaSciTech* 6, 105–121.
- Játariu, A.N., Danu, M., Peptu, C.A., *et al.*, 2013. Ionically and covalently cross-linked hydrogels based on gelatin and chitosan. *Soft Materials* 11, 45–54.
- Jin, R., Lin, C., Cao, A., 2014. Enzyme-mediated fast injectable hydrogels based on chitosan-glycolic acid/tyrosine: Preparation, characterization, and chondrocyte culture. *Polymer Chemistry* 5, 391–398.
- Jin, R., Moreira Teixeira, L.S., Dijkstra, P.J., *et al.*, 2009. Injectable chitosan-based hydrogels for cartilage tissue engineering. *Biomaterials* 30, 2544–2551.

- Kabir, S.M.F., Sikdar, P.P., Haque, B., *et al.*, 2018. Cellulose-based hydrogel materials: Chemistry, properties and their prospective applications. *Progress in Biomaterials* 7, 153–174.
- Karavas, E., Koutiris, E., Papadopoulos, A.G., *et al.*, 2014. Application of density functional theory in combination with FTIR and DSC to characterise polymer drug interactions for the preparation of sustained release formulations between fluvastatin and carrageenans. *International Journal of Pharmaceutics* 466, 211–222.
- Khare, A.K., Abraham, R.J.J., Appa Rao, V., Babu, R.N., 2016. Utilization of carrageenan, citric acid and cinnamon oil as an edible coating of chicken fillets to prolong its shelf life under refrigeration conditions. *Veterinary world* 9, 166–175.
- Khotimchenko, Y.S., Khozhaenko, E.V., Khotimchenko, M.Y., Kolenchenko, E.A., Kovalev, V.V., 2010. Carrageenans as a new source of drugs with metal binding properties. *Marine drugs* 8, 1106–1121.
- Kloda, L., Mikos, A.G., 2008. Thermoresponsive hydrogels in biomedical applications. *European Journal of Pharmaceutics and Biopharmaceutics* V68, 34–45.
- Kuznetsova, T.A., Andryukov, B.G., Besednova, N.N., Zaporozhets, T.S., Kalinin, A.V., 2020. Marine algae polysaccharides as basis for wound dressings, drug delivery, and tissue engineering: A review. *Journal of Marine Science and Engineering*.
- Ladet, S., David, L., Domard, A., 2008. Multi-membrane hydrogels. *Nature* 452, 76–79.
- Ladet, S.G., Tahiri, K., Montebault, A.S., Domard, A.J., Corvol, M.-T., 2011. Multi-membrane chitosan hydrogels as chondrocytic cell bioreactors. *Biomaterials* 32, 5354–5364.
- Lanzalaco, S., Armelin, E., 2017. Poly (*n*-isopropylacrylamide) and copolymers: A review on recent progresses in biomedical applications. *Gels* 3, 36.
- Laurienzo, P., 2010. Marine polysaccharides in pharmaceutical applications: An overview. *Marine Drugs*.
- Lee, Y.-E., Kim, H., Seo, C., *et al.*, 2017. Marine polysaccharides: Therapeutic efficacy and biomedical applications. *Archives of Pharmacological Research* 40, 1006–1020.
- Li, C., Wang, J., Yiguang, Wang, *et al.*, 2019. Recent progress in drug delivery. *Acta Pharmaceutica Sinica B* 9, 1145–1162.
- Li, J., Mooney, D.J., 2016. Designing hydrogels for controlled drug delivery. *Nature reviews. Materials* 1, 16071.
- Li, L., Ni, R., Shao, Y., Mao, S., 2014. Carrageenan and its applications in drug delivery. *Carbohydrate Polymers* 103, 1–11.
- Lin, C.-C., Anseth, K.S., 2009. PEG hydrogels for the controlled release of biomolecules in regenerative medicine. *Pharmaceutical Research* 26, 631–643.
- Liu, L., Gao, Q., Lu, X., Zhou, H., 2016. In situ forming hydrogels based on chitosan for drug delivery and tissue regeneration. *Asian Journal of Pharmaceutical Sciences* 11, 673–683.
- Long, J., Nand, A.V., Bunt, C., Seyfoddin, A., 2019. Controlled release of dexamethasone from poly(vinyl alcohol) hydrogel. *Pharmaceutical Development and Technology* 24, 839–848.
- Loret, C., Ribelles, P., Lundin, L., 2009. Mechanical properties of κ -carrageenan in high concentration of sugar solutions. *Food Hydrocolloids* 23, 823–832.
- Lu, H., Dai, Y., Lv, L., Zhao, H., 2014. Chitosan-graft-polyethylenimine/DNA nanoparticles as novel non-viral gene delivery vectors targeting osteoarthritis. *PloS One* 9, e84703. [e84703].
- Mahinroosta, M., Jomeh Farsangi, Z., Allahverdi, A., Shakoori, Z., 2018. Hydrogels as intelligent materials: A brief review of synthesis, properties and applications. *Materials Today Chemistry* 8, 42–55.
- Mo, F., Jiang, K., Zhao, D., *et al.*, 2020. DNA hydrogel-based gene editing and drug delivery systems. *Advanced Drug Delivery Reviews*. (In press). <https://www.sciencedirect.com/science/article/abs/pii/S0169409X20301022>.
- Moura, M.J., Faneca, H., Lima, M.P., Gil, M.H., Figueiredo, M.M., 2011. In situ forming chitosan hydrogels prepared via ionic/covalent co-cross-linking. *Biomacromolecules* 12, 3275–3284.
- Nanaki, S., Karavas, E., Kalantzi, L., Bikiaris, D., 2010. Miscibility study of carrageenan blends and evaluation of their effectiveness as sustained release carriers. *Carbohydrate Polymers* 79, 1157–1167.
- Nie, J., Wang, Z., Hu, Q., 2016. Chitosan hydrogel structure modulated by metal ions. *Scientific Reports* 6, 36005.
- Palmese, L.L., Thapa, R.K., Sullivan, M.O., Kiick, K.L., 2019. Hybrid hydrogels for biomedical applications. *Current Opinion in Chemical Engineering* 24, 143–157.
- Parhi, R., 2017. Cross-linked hydrogel for pharmaceutical applications: A review. *Advanced Pharmaceutical Bulletin* 7, 515–530.
- Park, H.-H., Ko, S.-C., Oh, G.-W., *et al.*, 2018. Characterization and biological activity of PVA hydrogel containing chitoooligosaccharides conjugated with gallic acid. *Carbohydrate Polymers* 198, 197–205.
- Park, Kyung, Lee, S., Joung, yoon ki, *et al.*, 2009. Thermosensitive chitosan-pluronic hydrogel as an injectable cell delivery carrier for cartilage regeneration. *Acta Biomaterialia* 5, 1956–1965.
- Patel, S., 2012. Therapeutic importance of sulfated polysaccharides from seaweeds: Updating the recent findings. *3 Biotech* 2, 171–185.
- Patel, V.R., Amiji, M.M., 1996. Preparation and characterization of freeze-dried chitosan-poly(ethylene oxide) hydrogels for site-specific antibiotic delivery in the stomach. *Pharmaceutical Research* 13, 588–593.
- Peniche, H., Peniche, C., Perez, J., 2018. Chitosan based self-assembled nanoparticles in drug delivery. *Polymers* 10.
- Picchioni, F., Muljana, H., 2018. Hydrogels based on dynamic covalent and non covalent bonds: A chemistry perspective. *Gels* 4, 21.
- Rajaram, A., Schreyer, D., Chen, D., 2015. Use of the polycation polyethylenimine to improve the physical properties of alginate-hyaluronic acid hydrogel during fabrication of tissue repair scaffolds. *Journal of Biomaterials Science. Polymer edition* 26, 1–23.
- Ranganathan, N., Joseph Bensingh, R., Abdul Kader, M., Nayak, S.K., 2018. Synthesis and properties of hydrogels prepared by various polymerization reaction systems. In: Mondal, M.I.H. (Ed.), *Cellulose-Based Superabsorbent Hydrogels*. Cham: Springer International Publishing, pp. 1–25.
- Rasool, A., Ata, S., Islam, A., *et al.*, 2020. Kinetics and controlled release of lidocaine from novel carrageenan and alginate-based blend hydrogels. *International Journal of Biological Macromolecules* 147, 67–78.
- Rhim, J.-W., Wang, L.-F., 2013. Mechanical and water barrier properties of agar/ κ -carrageenan/konjac glucomannan ternary blend biohydrogel films. *Carbohydrate Polymers* 96, 71–81.
- Rodríguez-Rodríguez, R., Espinosa-Andrews, H., Velasquillo-Martínez, C., García-Carvajal, Z.Y., 2020. Composite hydrogels based on gelatin, chitosan and polyvinyl alcohol to biomedical applications: a review. *International Journal of Polymeric Materials and Polymeric Biomaterials* 69, 1–20.
- Running, C.A., Falshaw, R., Janaswamy, S., 2012. Trivalent iron induced gelation in lambda-carrageenan. *Carbohydrate Polymers* 87, 2735–2739.
- Sahiner, N., Sagbas, S., Yilmaz, S., 2017. Microgels derived from different forms of carrageenans, kappa, iota, and lambda for biomedical applications. *MRS Advances* 2, 2521–2527.
- Salman, S., Asghar, S., Khan, I.U., *et al.*, 2020. Equilibrium, kinetics, thermodynamics and docking studies of Cu^{2+} ion adsorption over ion-exchange resin and kappa carrageenan blends in blood samples. *Pakistan Journal of Pharmaceutical Sciences* 33, 795–803.
- Sedayu, B.B., Cran, M.J., Bigger, S.W., 2019. A review of property enhancement techniques for carrageenan-based films and coatings. *Carbohydrate Polymers* 216, 287–302.
- Shen, X., Shamshina, J.L., Berton, P., Gurau, G., Rogers, R.D., 2016. Hydrogels based on cellulose and chitin: Fabrication, properties, and applications. *Green Chemistry* 18, 53–75.
- Shukla, P.S., Borza, T., Critchley, A.T., Prithiviraj, B., 2016. Carrageenans from red seaweeds as promoters of growth and elicitors of defense response in plants. *Frontiers in Marine Science*.
- Stuurman, F.E., Nuijen, B., Beijnen, J.H., Schellens, J.H.M., 2013. Oral anticancer drugs: Mechanisms of low bioavailability and strategies for improvement. *Clinical Pharmacokinetics* 52, 399–414.
- Talebian, S., Foroughi, J., 2020. Chapter 7 – Intelligent drug delivery systems. In: Seyfoddin, A., Dezfouli, S.M., Greene, C.A.B.T.-E.D.D.S. (Eds.), *Woodhead Publishing Series in Biomaterials*. Woodhead Publishing, pp. 163–184.

- Tang, M., Lei, Y., Wang, Y., Li, D., Wang, L., 2021. Rheological and structural properties of sodium caseinate as influenced by locust bean gum and κ -carrageenan. *Food Hydrocolloids* 112, 106251.
- Torres, M.D., Chenlo, F., Moreira, R., 2017. Thermal reversibility of kappa/iota-hybrid carrageenan gels extracted from *Mastocarpus stellatus* at different ionic strengths. *Journal of the Taiwan Institute of Chemical Engineers* 71.
- Tziveleka, L.-A., Ioannou, E., Roussis, V., 2019. Ulvan, a bioactive marine sulphated polysaccharide as a key constituent of hybrid biomaterials: A review. *Carbohydrate Polymers* 218, 355–370.
- van de Velde, F., Antipova, A.S., Rollema, H.S., *et al.*, 2005. The structure of κ/ι -hybrid carrageenans II. Coil–helix transition as a function of chain composition. *Carbohydrate Research* 340, 1113–1129.
- Varshosaz, J., Tabbakhian, M., Salmani, Z., 2008. Designing of a thermosensitive chitosan/poloxamer in situ gel for ocular delivery of ciprofloxacin. *The Open Drug Delivery Journal* 2.
- Yegappan, R., Selvaprithiviraj, V., Amirthalingam, S., Jayakumar, R., 2018. Carrageenan based hydrogels for drug delivery, tissue engineering and wound healing. *Carbohydrate Polymers* 198, 385–400.
- Zarrintaj, P., Manouchehri, S., Ahmadi, Z., *et al.*, 2018. Agarose-based biomaterials for tissue engineering. *Carbohydrate Polymers* 187, 66–84.
- Zhang, H., Fan, T., Chen, W., Li, Y., Wang, B., 2020a. Recent advances of two-dimensional materials in smart drug delivery nano-systems. *Bioactive Materials* 5, 1071–1086.
- Zhang, K., Feng, W., Jin, C., 2020b. Protocol efficiently measuring the swelling rate of hydrogels. *MethodsX* 7, 100779.
- Zia, K.M., Tabasum, S., Nasif, M., *et al.*, 2017. A review on synthesis, properties and applications of natural polymer based carrageenan blends and composites. *International Journal of Biological Macromolecules* 96, 282–301.

Multifunctional Polymer Matrix Composites

Sajid Asghar and Haroon K Syed, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

Kai Bin Liew, University of Cyberjaya, Cyberjaya, Selangor, Malaysia

Ikram U Khan and Saad Salman, Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, Government College University Faisalabad, Faisalabad, Pakistan

© 2021 Elsevier Inc. All rights reserved.

Introduction

The current unparalleled boom in the field of material sciences has never been witnessed in the known history of humanity. The industrial revolution and the many feats achieved in different avenues of life have only been possible due to the continuous innovations in the development of unique materials, their manufacturing, processing, and identification of unconventional combinations with various properties. Polymer matrix composites are a class of materials that have been the keystone of this revolution. A material blend made by the dispersion of one or more physically and chemically distinctive constituents into a polymer matrix is termed as polymer matrix composite and could be called multifunctional polymer matrix composite if it possesses additional properties than those of the main matrix former alone (Curtis, 1996). These composites have also been loosely called intelligent or smart materials. The dispersant component or filler is usually scattered in the form of fibers, tubes, capsules or particles in a continuous polymer matrix. The choice of dispersant components and the processing treatments during the blending process guide the emergence of the so-called multifunctionality. Furthermore, size, shape, and arrangement of the discontinuous phase is pivotal in the scope of multifunctionality.

Initially, polymer composites were designed to achieve the ability to withstand maximum load for structural purposes (non-functional) in the fields of civil and mechanical engineering. The functional attributes (non-structural) were then incorporated with the aid of specific devices. This not only compromised the structural features but also led to underperformance of the functional devices. The maintenance of such equipment or structures was hectic and time consuming thus leading to a hefty increase in overall cost. The emergence of multifunctional polymer composites allowed the integration of various functional features in the structural materials without any substantial gain in the structural mass or loss in their mechanical prowess (Christodoulou and Venables, 2003). The structural traits of an ideal multifunctional polymer matrix composite include ability to bear passive load, durability, malleability and resistance to deform upon sudden or continuous exposure of thermal, mechanical, chemical, or biological stresses (Ali and Andriyana, 2020). Whereas, a range of functional characteristics can be included such as thermal, electrical or sound insulation, flame retardation, energy generation and storage, electromagnetic interference shielding, self-repairing, sensing of mechanical or chemical phenomenon, ability to control contamination, and biocompatibility and biodegradability for health monitoring, drug delivery, antimicrobial activity and wound healing applications.

This article is an effort to concisely describe the various functionalities of these useful materials along with nature, properties, and maneuvering of the fillers that give rise to the desirable traits. In addition, the latest striking findings in the key applications of the multifunctionalized polymer matrix composites have also been discussed.

Insulation Functionality

Electrical Insulation

The scale of size has significantly moved towards the lower numbers in the past few decades for the high-end application electronics, thanks to the excellence in materials research. This downsizing structural trend has facilitated unprecedented growth in many industries, such as computation, telecommunication, transportation, energy storage, renewable energy generation, civil and mechanical engineering, and warfare. However, the race to miniaturize the appliances has led to crowding of various functional electrical or electronic parts in limited dimensions. Electrical insulation of the parts is needed, in order for such systems to be functional. The use of polymeric composites is quite popular in devising such parts as the polymeric matrices are usually less conductive to electrical and thermal energies. Nonetheless, due to thermal insulation and poor heat dissipation of the simple polymeric composites, there arises the problem of overheating. Overheating, if not dealt with, can lead to short-circuits, unreliable performance, reduced operational life, and high maintenance cost.

Significant efforts have been made to develop the multifunctional polymer composites with thermal conductivity with electrical insulation properties. Different kinds of conductive fillers have been tested in polymer composites for thermal conductivity. Use of metallic or inorganic materials as fillers was considered as the natural choice, but, the degree of dispersion of these fillers within the polymer matrix is difficult to control due to poor filler-matrix interaction. The weaker interaction at the interface of metallic fillers and matrix polymers causes filler aggregation and raises the interfacial thermal resistance, thus, leading to sub-optimal thermal conductivity performance of such composites. Raising the filler levels in the overall composition of composites can overcome this issue but will compromise the electrical insulation and mechanical strength of the composites (Guo *et al.*, 2020).

Carbon based fillers (carbon/graphene nanotubes) possess excellent conductivity properties and have also been applied for improving the thermal conductivity of the polymer composites, but, they also have good electrical conductivity, making them less

desirable for such applications (Song *et al.*, 2019). Modification of carbon nanotubes could help in improving their electrical insulation attribute. Fluorinated carbon nanotubes when grafted with poly (methyl methacrylate) showed better dispersion within the matrix of the polymer, reduced interfacial thermal resistance and better electrical insulation (Wang and Wu, 2019). Techniques used for designing anisotropic nanofillers-based electrically insulated polymer composites with better thermal conductivity create materials with heat flow in one direction only, hence, limiting the overall efficiency of the composites. Polymer matrix composite containing 3 D polydopamine coated graphene oxide structure as filler was shown to possess electrical insulation and the ability to dissipate the thermal energy in all planes. The 3D construct ensures lower interfacial thermal resistance by minimizing the polymer/filler interfaces (Yuan *et al.*, 2019).

Boron-nitride, in the form of nanoparticles, nanosheets, nanotubes or nanoribbons, has emerged as an excellent nanofiller for thermally conductive polymer composites. Other than thermal conductivity, boron nitride is also resistant to mild acids and corrosion, and provides minimal friction; making it as a suitable material for filler in polymer composites (Li *et al.*, 2020a; Zou *et al.*, 2019). On the other hand, higher loading of boron-nitride as a filler are required for the desirable thermal conductivity. Use of multiple fillers or hybrid fillers than a single filler could be a more viable option in dealing with heat dissipation by electrically insulated composite materials. Combinations of boron-nitride with other fillers such as carbon based materials or glass fibers have been reported to improve the thermal conductivity of polymer composites while maintain the required level of electrical insulation (Ohayon-Lavi *et al.*, 2020; Tang *et al.*, 2019; Zhang *et al.*, 2019).

Thermal Insulation

In contrast to the electronics industry, thermal insulation is highly desirable for construction, machine performance, goods storage, transportation, and packaging purposes. Currently, the governments are striving to make thermal insulation as an integral part of the construction industry to conserve energy. The global realization about the hazardous ecological outcomes pertaining to the use of fossil-fuels for energy generation has been the driving force for the design of efficient thermal insulator materials. Thermal insulation is also desirable for personnel safety, proper storage and transportation of thermolabile goods, medicine or biological samples (Verma and Singh, 2019; Aditya *et al.*, 2017; Chatterjee and Pandey, 2003).

The highly porous polymeric composite constructs having high mechanical strength and lightweight, such as foams, are desirable for the thermal insulation. Recently, carbon nanotubes enforced polypropylene composites-based foam showed higher mechanical strength with better control over pore structure for better thermal insulation (Zhao *et al.*, 2020). Decrease in thermal insulation capability of the foams at higher temperature stress makes them unsuitable for special purposes. Polymer composite aerogels, air filled polymeric composites, are durable, light-weight and have greater thermal insulation capacity even at higher temperatures. Inorganic filler cross-linked polyimide aerogels demonstrate tunable cell structure linked to the degree of cross-linking, increased mechanical strength, and persevered thermal insulation at elevated temperature (Fan *et al.*, 2019). Carbon-based materials (carbon nanotubes or graphene fibers) have high mechanical strength but good conductivity properties therefore their use in thermal insulation material is less than desirable. Use of natural fibers as fillers in the foams rather than the carbon based fibers is more beneficial as natural fibers are cheap and possess inherent thermal inertness, lower densities, and porous structure along with reasonable mechanical strength (Floreana and Manea, 2019).

Thermal aging, reduction in performance of thermal insulation materials over a period of time, is needed to be addressed in the design of the advanced polymeric composites. It can originate from the changes in the nature of material due to damage to the polymer construct, porous structure shrinkage, hygroscopicity, microbial degradation or biodegradation of the natural fibers, and leakage of entrapped air or gasses from the aerosol cells (Fraleoni-Morgera and Chhikara, 2019; Takagi, 2019). Generally, material strength and durability are compromised by the addition of various fillers (Charles *et al.*, 2020).

Noise Reduction

The facilitation and the luxurious life style owing to the industrial growth has introduced many detrimental factors into the daily lives of the current era. One of such factors is the uncontrolled and unwanted noise generated from industrial machines, construction work, automobiles, aeroplanes, and ships. The health threats of noise have been considerable, and it is even recognized by the world health organization. These effects include but not limited to auditory malfunction, cardiac issues, central nervous system disorders, and behavioral changes (Goines and Hagler, 2007; Stansfeld and Matheson, 2003). The deleterious effects of noise have also been evident in different animal communities (Senzaki *et al.*, 2020).

Traditionally, glass have been extensively used for the acoustic control in buildings. However, polymer composites have been investigated for noise reduction purposes. Degree and nature of porosity (granular, cellular, or fibrous) of the composite plays an important role in the reduction of noise amplitude. Polymer matrices supplemented with high density minerals, glass fibers, carbon nanotubes, graphite platelets, and natural fibers show promising noise reduction properties (Chuang *et al.*, 2016; Berardi and Iannace, 2015). The length of the fibers, size of the nanoparticles or platelets, filler microstructure, orientation of fibers, and the overall filler content in the polymer composite influence the extent to which a certain type of noise can be reduced (Kumar *et al.*, 2020).

Inclusion of high density fillers such as minerals in the polymer composites reduces the vibration in the material due to greater mass, thus, reduction of noise is possible from such composite systems. Increased noise reduction is also related to the higher degree of dispersion of the dense minerals within the polymer matrix (Ersoy, 2020). However, dense materials increase the mass of

the final product which is considered undesirable in various applications. Insertion of glass fiber felt in the form of multiple layers in the polymer matrix generate more voids which ensures better sound absorption (Xue *et al.*, 2019). Similarly, entrapment of air within the glass fiber reinforced polymer matrix dampens the sound better than the one without air bubbles (Shin *et al.*, 2020).

Natural fibers or by-products of crops have marvelous noise dampening potency (Kolya and Kang, 2020). Now-a-days, the use of natural materials or by-products is being emphasized in construction industry for industrial waste management and encouragement of use of renewable resources to attenuate the impact of synthetic materials on the environment. The nature of the fiber and its size has major impact in the sound dampening potential of the polymer composites made with these renewable sources (Marques *et al.*, 2020a,b; Tiuc *et al.*, 2019). Including multiple fillers in the polymer matrix gives better noise reduction than the polymer composites with a single filler (Kim *et al.*, 2013). Combination of natural and synthetic fillers in the polymer matrices are beneficial for acoustic application due to the lower costs and better mechanical and structural properties (Gokulkumar *et al.*, 2019; Prabhu *et al.*, 2019).

Vibration Damping

Vibrations are a serious cause of harm for both structures and machines. The integrity and durability are affected on prolonged exposure of vibrational energy. Whereas, performance and experience or comfort of mechanical, electronics, or transporting vehicles are markedly downgraded by the vibrations. Passive damping of vibrations by use of materials is considered cheap and doable rather than using active damping by specific devices (Chung, 2001). Viscoelasticity of the materials is considered important factor for designing damping materials (Zhou *et al.*, 2016). Metals, glass, carbon based material, and natural fibers have been employed to make damping polymer composites (Tang and Yan, 2020).

Slip-stick phenomenon of carbon nanotubes within the polymer matrix was identified as the mechanism of efficient damping by carbon enforced polymer composites (Ajayan *et al.*, 2006). This effect is more prominent when the nanotubes have abysmal interaction with the polymer matrix. Recently, Joy *et al.* (2020) showed that inner oscillations of the multiwalled carbon nanotubes within the polymer composite depends upon the nanoscale architecture affect the damping efficiency. The graphene nanoplatelets enforced epoxy polymer composites also displayed better vibration damping potential (Rafiee *et al.*, 2019). Use of piezoelectric metal wires in tandem with carbon nanotubes in matrix composite were demonstrated to dissipate the vibrational energy more efficiently by additional conductivity phenomenon (Groo *et al.*, 2019). The renewable source, good viscoelasticity, and hollow nature of natural fibers also make them suitable for use in vibration absorbing matrices (Takagi, 2019).

Flame Retardation

Direct or indirect fire accidents are the most common and dangerous threat to the life, environment, machines and structures. Despite the multidimensional usefulness of the polymer composites, these materials are most vulnerable to fire due to the hydrocarbon or petrochemical origin (Bar *et al.*, 2015). The flammability of the polymeric composites, once initiated, is a self-sustaining attribute. Polymers are prone to degradation or pyrolysis in the presence of sufficient heat and oxygen; subsequent release of the flammable gases further promotes the extensive burning of material by exploitation of the available oxygen, thus, strengthening the overall cycle (Babu *et al.*, 2020). In order to impart flame retardancy, fillers are used that can improve the heat tolerance of the polymer matrix or reduce the emission of inflammable gases or increase the formation of char (a non-flammable byproduct of combustion formed along with gases), or release the gases that are non-flammable (Bar *et al.*, 2015).

Carbon nanotubes or graphene fibers are inherently non-flammable and have good heat tolerance, but, fire events usually produce high heat levels, so requiring further modification of the material to improve the fire retardancy. Use of phosphorous modification is useful in improving the fire retardancy of graphene enforced polymer composites by improving thermal endurance, increased char formation (non-flammable byproduct of combustion), and decreased smoke generation (Cao *et al.*, 2019). Use of magnesium hydroxide as anti-dripping agent (materials that decrease the flow of the polymers upon heating) in the carbon fiber reinforced phosphorous modified polymer composites was reported to significantly amplify the fire resistance of the designed composites (Javaid and Afzal, 2018). Layered double hydroxides have been shown to improve the flame retardancy of the polymer composites by improving thermal resistance, promoting emission of non-flammable gases, and making a carbonized layer (Luo *et al.*, 2020). Recently, it was demonstrated that fire resistance of the intumescent flame retardants (thermoreponsive agents that form a flame and heat-resistant swellable carbon layer) by inclusion of metal oxides (Gao *et al.*, 2020). Metal organic frameworks as fillers are also gaining significant attention due to their ability to limit the spread of fire by forming char barrier, absorbing the pyrolysis products, and suppressing the toxic and flammable gases (Pan *et al.*, 2020).

Energy Harvesting, Storage, and Conservation

Energy Generation

The massive energy generation in the last century by burning fossil fuel has caused significant ecological disturbances to conclude that the future of humanity and earth is at stake. This realization has been continuously spreading across the globe to curb the

consumption of hydrocarbons in every aspect of life and has fueled the search for the generation of energy from the more natural processes. Solar, wind, magnetic, tribological, electrostatic, and piezoelectric and many more phenomenon are being explored aggressively in this regard (Bai *et al.*, 2018).

The use of polymeric composites is increasing in the recent studies for efficient harvesting of energy. Graphene as a carbon based conducting material possesses interesting properties and has been used in the form of sheets for the polymeric photovoltaic cells. Different modification approaches have been used to further enhance its applications (Tiwari *et al.*, 2020). Thermoelectric harvesting has also been recently studied with graphene based hybrid polymeric composites owing to the good conductivity of graphene (Liu *et al.*, 2020). Due to the boost in demand of wearable gadgets, search for the elastic polymer composites for thermoelectric harvesting is also increasing. Biomedical monitoring of diseases by use of miniature electronics is pushing the horizon of material development. Brittle polymers can be functionalized into more elastic and adaptable structures for such applications (Kim *et al.*, 2020). Piezoelectric energy harvesting (converting vibrations or mechanical energy into electricity) by polymeric composites incorporating metal organic framework have been investigated for the self-sustainable monitoring of the arterial pulse (Hadavi Moghadam *et al.*, 2020). Similarly, metal oxide nanoparticles in tandem with multiwalled carbon nanotubes incorporating polymer matrix film as an energy harvester on cardiac pacemaker has been studied (Xu *et al.*, 2020).

Energy Storage

Storage of energy is as important as the energy harvesting from various renewable source. Poor energy storage has been the bottle neck for the development of energy sector in recent years. Polymer composites have been applied for the energy storage devices as batteries (chemical energy storage devices) or capacitors (electrical energy storage devices). However, the use of fillers for efficient energy storage is possible in quantities that downgrade the structural performance of the polymer composites (Chung, 2001). Therefore, the energy storage is quite challenging for the material scientists.

The dielectric layer in capacitor is of prime importance for energy storage as it should be resistant to electrical conductivity and should have amiable interfacial interaction within the conductive polymer matrix. Dielectric polymer composites with sufficient thermal forbearance is key to the success of energy storage (Zhou and Wang, 2020). The layering of the polymer composites with the nanowires of ceramic materials in a gradient architecture showed better control over the breakdown strength and the dielectric properties necessary for the energy storage. The marked improvement in the energy density was made possible by the layered interfacial electric gradient and the barrier sheets to limit the charge leakage (Wang *et al.*, 2020b). The design of polymer composites electrodes for batteries require the interplay of both conductivity and structural integrity. Ionic liquids functionalized polymer composites are also being used as electrodes for batteries (Correia *et al.*, 2020). Graphene nanoplatelets functionalized bimetallic polymer composites when used as electrode in lithium ion battery demonstrate enhanced electrochemical performance due to improved conductivity and shortened lithium ion migration path (Kang *et al.*, 2020).

Electromagnetic Interference Shielding

Dependence of humans on the use of computational devices has rapidly extended from complex devices to the daily life activities. Almost all such electronic machines emit radiations known as electromagnetic waves. Initially, these radiations were identified to interfere with the functionality of other electronics; however, with the every passing day, the deleterious health and behavior effects of these radiations emitted from the excessive utilization of the so-called useful gadgets are coming into light. The ability of the multifunctional polymeric composites to absorb or reflect the electromagnetic radiations has been exploited extensively for electromagnetic interference (EMI) shielding (Chandra *et al.*, 2019). Earlier studies identified that incorporation of short metal fibers in the polymeric coatings for shielding against electromagnetic radiations is useful because of the good adhesion of the coated matrices on the surfaces. The choice of metal depends on the density, ductility, and conductivity (Bagwell *et al.*, 2006). Use of high conductivity fillers in the nanosize range has been preferred and a range of fillers with different attributes have been reported for the EMI shielding in the literature. Greater surface area, higher interfacial interaction in the matrix due to better dispersion, morphological characteristic of filler, and thickness of the shielding material are as important as the nature of the filler (Wanasinghe *et al.*, 2020).

Self-Healing

Nature has always been a source of inspiration for the material scientists to strive for the biomimetic designs or to incorporate features into the materials that exist in the natural settings only. Restoration of a material to its original form, on its own, upon damage from mechanical or thermal stress is termed as self-healing. Although, the natural self-healing in a living organism is too complex, the design of materials is shifting from conventional stress tolerance to the self-repairing (Trask *et al.*, 2007). The self-healing attribute in the polymer composites cannot be achieved without incorporation of stimuli-responsiveness. These stimuli could be mechanical load or impact, temperature, electromagnetic radiations, or light (Hia *et al.*, 2016).

Dispersion of the healing agent filled micro or nanocontainers across the polymeric matrices has been widely employed for the design of self-healing materials. The release of the healing material occurs in response to the stress to restore or minimize the

damage. The containers could be layered to contain the self-healing reactant components within the same container and then dispersed in the polymer matrix. However, the size of such layered containers needs to be minimized along with the residual water content for better restoration of the matrix (Cao *et al.*, 2020a). Double walled capsules have been designed for higher loading of the healing agent to obtain better healing efficiency (Ma *et al.*, 2020). Fabrication of organic coatings of polymer matrix composite containing natural biomass based capsules for healing against scratching and photodegradation of surfaces can be achieved (Qian *et al.*, 2020). Co-encapsulation of reactive liquids or solvents for self-healing could restore the electro-mechanical characteristics of the polymer composites (Zamal *et al.*, 2020). Most of the self-healing materials only restore the structure for limited number of accidental exposures. Increasing the healing capability of the materials in terms of handling of multiple stress incidents could lead to design of self-sustaining structures with least maintenance required. Design of containers with numerous storage units of healing agent has been reported to increase the repeatability of healing phenomenon. The containers are designed to hierarchically release the healing agent layers thus making the material sustainable for multiple healing cycles (Xue *et al.*, 2020).

Other than limited cycles of healing due to the slender healing agent storage capacity, use of healing agent filled containers in the polymer matrix might not yield the effective restoration due to the uneven distribution of these container in the matrix. In addition, after the release of the healing agent, the empty shell of the container could become a structural defect or reduce the efficiency of the overall healing. Shape memory polymers and thermoplastic polymers, alone or in combination, are also being used to make self-repairable functional polymer matrix composites. Jony *et al.* designed a biomimetic self-healing polymeric composite where the shape memory polymer was used to close the cracks, and the thermoplastic polymer induced the healing (Jony *et al.*, 2019). Similarly, thermoplastic poly-caprolactone and shape memorizing polyurethane can fix the impairment in carbon reinforced polymeric composite caused by delamination (Jony *et al.*, 2020). Use of thermoplastic filler layers for healing in matrix composite might lead to generation of voids that can negatively impact the structural integrity or compromise the structure repair. The design of polymer composites where the healing filler reversibly interacts by chemical bonding or other molecular interactions (electrostatic, hydrophobic or hydrogen bonding) with the matrix polymer could lead to a viable self-healing design. Amidated carbon fiber reinforced polymer matrix serves the purpose of the self-repair by hydrogen bonding (Wang *et al.*, 2019). Modified Graphene oxide enforced polymer matrix composite also repairs itself by hydrogen bonding interaction with the polymer matrix (Du *et al.*, 2020). Catalyst-free reversible chemical bonding based self-healing by Diels Alder reaction has been extensively studied. This thermo-sensitive reversible chemical reactions has been applied in various polymer matrix systems including fiber-reinforced plastics, cellulose based composites, polymeric resins, epoxy composites, polyurethane coatings and many more (Cao *et al.*, 2020b; Ouyang *et al.*, 2020; Sahu and Bhowmick, 2020; Shahidzadeh *et al.*, 2020; Wu *et al.*, 2020).

Sensing Functionality

The conductive ability of the multifunctional polymer matrices has been found to respond to various external stress phenomenon, and it can be translated into detecting or sensing the nature and the magnitude of such stimuli. The discrete sensing functionality of polymer composites is crucial for the proper working, maintenance, and mending of the devices or structures (Chen *et al.*, 2020).

Mechanical Sensing

Sensing of strain or pressure from a mechanical stimulus has been applied for the improvements in the transportation industry, civil engineering, robotics, human-machine interface, and health tracking devices. The good dispersibility and filler-matrix interaction yields better sensor performance. Increasing the dispersion and the interfacial interplay of the carbon nanotubes in the thermoplastic polymer by non-covalent interactions increases the sensitivity of the 3-D printed piezoresistive sensors that can detect human motions and stress due to mechanical load (Xiang *et al.*, 2020). Ionic liquids can also be used to improve the dispersion of the conductive carbon nanofillers in the polymer matrix for enhanced intermolecular interactions and more sensitive detection of stress and material deformity (Gariya *et al.*, 2020). Dynamic polymer matrix with a conductive filler that rearranges its network at different strain rates, such as flowy to fixed state, can be used to devise tactical sensors. Such approach uses the fixing of dispersed conductive fillers at the application of stimulus by phase shifting of the polymer matrix, which hinders the conductivity but is regained upon stress removal due to redispersion of the filler in the dynamic polymer network (Zhou *et al.*, 2020). Similarly, dynamic polymer network can be utilized by catalytic conversion of the fixed polymer matrix, which has good sensor functionality even at lower loadings of the conductive segregated nanofiller network (Yuan *et al.*, 2020).

Chemical Sensing

Presence of certain chemicals in the form of ions, vapors, gases, or humidity can be sensed upon their interaction with the smartly designed polymer composites. Chemical sensing is very valuable for detection of warfare chemicals, contamination, biomedical applications, food and pharmaceutical storage, and protection of natural reservoirs. Hydrocarbon soluble polymer matrix functionalized with carbon fibers can detect the presence of the hydrocarbon pollutants originating from leakages or accidents in the petrochemical industry. The interaction of the hydrocarbon material produces structural deformities in the polymer matrix composite and leads to changes in material conductivity (Seshadri *et al.*, 2020). Potentiometric sensors for detection of metal ions was fabricated by inclusion of multiwalled carbon nanotubes in

the lignin-based polymer matrix. Specific interaction of the polyphenolic components of the lignin with the copper ions was attributed to the selective sensing of the metal ions (Gonçalves *et al.*, 2020). Titanium oxide nanoparticles functionalized polyaniline matrix coating was applied to glass-carbon electrode to detect the real-time presence of a harmful industrial pollutant, diaminobenzene (Karim *et al.*, 2020). Polyaniline-multiwalled carbon nanotube hierarchical composites showed high sensitivity detection of low levels of nitric oxide and ammonia gases (Zhang *et al.*, 2020b). Similarly, Cotton fiber-polyaniline multifunctional composites were fabricated for selective sensing of ammonia gas (Zhang *et al.*, 2020c). Humidity detection for sensitive food and pharmaceutical applications is necessary to avoid decomposition of the products. Polymer composite films of polyvinylidene when functionalized with barium-titanium nanoparticles serve as good detectors of humidity based on corresponding changes in the dielectric capacitance (Mallick *et al.*, 2020). Polymer composites for chemical sensing applications are prone to the environment conditions such as temperature and humidity. Moreover, selectivity, competitive interaction of different analytes and sensitivity to detect lower quantities of analytes (specifically parts per billion) are the major hurdles in the design of chemical sensors from polymer composites (Pawar *et al.*, 2020).

Contamination Control

The expansive industrialization has led to contamination of natural resources with innumerable pollutants. The constant realization of contamination in past few decades has not only moved the scientific, industrial, and governmental organizations to look for less hazardous, renewable, and waste management materials but also for the control of the pollutants for the recovery of natural ecological balance and habitat (Jaspal and Malviya, 2020). Hollow fibrous polymer composite membranes functionalized with iron oxide nanoparticles and graphene oxide nanosheets possess high surface oxygen groups and have the ability to remove the carcinogenic dichlorophenols from water with excellent reusability (Modi and Bellare, 2020). Porosity of the polymer composite membranes for higher surface area and the number of functionalized groups are very important features in the decontamination functionality of the membranes. Reduced graphene oxide functionalization of polyimide to yield nanofibrous membrane shows excellent stability under harsh environment and can remove oil from the polluted water reservoirs (Zhang *et al.*, 2021). Polymer matrix nanofibrous filters made by functionalization with either nitrogen containing or phosphorous containing compounds can treat the uranium contaminated water by electrostatic interactions in a pH-dependent manner (Johns *et al.*, 2020). Other than adsorption of heavy metals, filter membranes can be made to perform catalytic degradation of the organic pollutants such as dyes. Zhang *et al.* designed polymer composite based highly microporous membranes functionalized with polydopamine coated ferroferric oxide nanoparticles to efficiently decontaminate water by simultaneously removing heavy metals and catalytic degradation of the organic wastes. The catalytic degradation is achieved due to the filler polydopamine coating with phenoquinone moieties that induce degradation by promoting electron transfer (Zhang *et al.*, 2020a). Natural polymeric composites of cellulose have been extensively studied for making nanofibrous membranes for water treatment (Tshikovhi *et al.*, 2020). Air decontamination can also be achieved from cellulose based matrix composite functionalized with metal organic framework in chitosan. This highly porous filter paper showed the ability to adsorb the air-borne particulate matter (Nie *et al.*, 2020).

Biomedical Applications

A significant amount of research focus across the globe is to exploit the advancements in the material research for biomedical applications. Multifunctional polymer matrices has paved the way for development of flexible devices that can meet personalized biomedical needs. Not only natural materials but also the synthetic materials have been designed with ample biocompatibility and biodegradability, thus making them suitable for health related applications. The low cost, light weight, huge surface area, and the possibility of multiple modifications and functionalization make polymer composites ideal for application in a range of biological applications (Eslahi *et al.*, 2020).

Antimicrobial Activity and Wound Healing

The growing threat of microbial diseases, the emerging pandemics, development of antimicrobial resistance, and increasing incidences of nosocomial infections due to surface growth of microbes demand design of safe antimicrobial materials for building and devices (Milazzo *et al.*, 2020). Areca fiber reinforced epoxy resin polymer matrix composite functionalized with neem oil and silica nanoparticles show antimicrobial activity against several microbial strains (Samuel *et al.*, 2020). Polymers containing amine groups usually show antimicrobial activity. Chitosan and pullulan composite films display sufficient antimicrobial activity for the films intended for food packaging (Li *et al.*, 2020b). Chitosan and pluronic F127 composite hydrogel when loaded with copper oxide nanoparticles show antibacterial activity against both gram positive and negative bacteria, thus making it a suitable candidate for wound dressing (Jayaramudu *et al.*, 2020). Similarly, chitosan-tigecycline composite films showed significant antibacterial potential against different bacterial strains (Menazea *et al.*, 2020). Interpenetrating hydrogel network loaded with silver nanoparticles of natural gum, acrylamide and acrylic derivative showed both antibacterial and antifungal activities (Sharma *et al.*, 2020). Microbial contamination of surfaces at home or hospital and medical devices such as stents and catheters is an aggressively emerging threat to human health. An antimicrobial polylactic acid film for surface applications was functionalized with polyheamethylene guanidine hydrochloride grafted starch

microparticles. Non-leaching behavior of the films was observed that makes it suitable for surface applications as bacteria will be killed upon contact with the surface (Sharma *et al.*, 2020). An acrylate based cationic polymer film functionalized with titanium oxide nanoparticles for the construction of inner building walls has been shown to possess antimicrobial properties owing to both cationic film and the incorporated filler nanoparticles (Wang *et al.*, 2020a). Improvement in hydrophilicity and swelling behavior of the dressings made with polymer composites show promising control over wound closures. Biopolymer matrix composites based films with good mechanical properties and antibacterial activity have been made for the wound healing applications (Rahmani *et al.*, 2020). Natural polymer composite dressings possessing the functionality for adhesion of cellular components such as red blood cells and platelets are considered effective for closure of wounds associated with hemorrhage (Biranje *et al.*, 2020). Metal nanoparticle incorporated biopolymer composite hydrogel dressings with sufficient antibacterial activity are also potential material candidates for wound healing applications (Gou *et al.*, 2020).

Health Monitoring

One of the current focus of research in healthcare industry is to develop approaches for real-time health monitoring and non-invasive detection of disease biomarkers. Wearable devices containing biosensors are manufactured to monitor the vital signs of patients or athletes. Use of multifunctional polymer composites as biosensors is quite attractive as these materials offer energy storage needed for device operation and stimuli responsiveness to various biological phenomenon (Prajapati and Kandasubramanian, 2019). Polymer matrix composite can be functionalized to measure the body temperature. Temperature changes usually alter the conductivity or capacitance in the functional polymer composites, which can be used for sensing of thermal changes. Dan and Elias demonstrated the thermal sensing performance of reduced graphene oxide functionalized flexible polyhydroxybutyrate matrix composite. Hydrophobic nature of the composite makes it water-resistant thus expanding the thermal monitoring in wet conditions too (Dan and Elias, 2020). Nanofibrous porous composite of Graphene nanosheets with polyamide was developed as a flexible wearable sensor with diverse applications. The designed polymer composite displayed temperature sensing, human motion sensing, and even the physiological electrocardiogram monitoring (Lu *et al.*, 2020). Amperometry based sensing of various biochemical entities in the biological fluids by polymer matrix composite based electrodes has been investigated in recent research studies. A nanohybrid electrode of phototungstic acid-polydiphenylamine-zinc oxide-glassy carbon showed sensitivity for detection of glucose by amperometry (Muthusankar *et al.*, 2020). Similarly, glucose, uric acid, and nitrite in various biological fluids were detected by graphene functionalized polylactic acid electrode fabricated by 3D printing. Glucose was determined in blood, whereas, uric acid and nitrite were detected in saliva and urine samples (Cardoso *et al.*, 2020).

Drug Delivery

Polymer composite matrix can be used as a vehicle for the delivery of drugs inside human body for therapeutic purposes. Biocompatibility and biodegradability are the pre-requisites for drug delivery, whereas, presence of porous structure, structural voids, and functional moieties are advantageous for ample loading capacity of diverse nature of pharmaceutical active ingredients. These materials could also provide protection to drug against chemical or biological degradation, controlled release, and stimuli-responsive organ targeting owing to multiple functionalization. Metal oxide framework functionalized polymer composites have great potential as drug carriers (Chapman *et al.*, 2020; Osterrieth and Fairen-Jimenez, 2020). Gandara-Loe *et al.* (2020) showed that nanocomposite films of metal oxide framework in polymer matrix could be exploited for ocular drug delivery. The versatile fabrication techniques, diverse structural traits, and ease of modification and crosslinking in polymer composites allows facile morphing of these composites into various shapes and sizes. Different shapes and sizes have variable properties and benefits in drug delivery as the interaction of carrier with the biological membranes can be modified on the basis of shape. Vatankhah *et al.* (2020) studied the changes in drug release pattern corresponding to the shape of acrylate composite particles. Polyvinyl alcohol cross-linked chitosan microneedle patches showed substantial controlled release of diclofenac sodium for transdermal application. Degree of cross-linking is crucial in determining the mechanical strength, drug loading, and release performance of designed polymer composite delivery system (Dathathri *et al.*, 2020).

Summary

Multifunctional polymer matrix composites find diverse applications in almost every domain of material science. Use of functionalized fillers has driven the limitless applications and paved ways for new technological advancements. Recently, a noticeable shift in the research of materials is the use of renewable and natural materials to address the ever-increasing issue of environmental safety. The use of natural fibers as polymers, reinforcements or fillers in the polymer composite matrix has advantages in many applications, but it is still too early for natural materials to replace the synthetic one. For example, natural fiber functionalized polymer composites are useful in insulation but cannot be applied for fire retardancy or conductivity applications. Although, synthetic polymer composites also suffer from degradation; natural fibers are more prone to microbial degradation and can easily absorb moisture which can compromise the overall material performance. Conversely, natural polymers are irreplaceable in biomedical applications ranging from health monitoring to drug delivery. Generally, material strength and durability are

compromised by the addition of various fillers. Use of nanosized fillers is revolutionizing the multifunctionalization approach, however, morphology, architecture, size, and dispersion of these fillers need careful attention for each specific functionality. The advanced research in the multifunctional polymer matrix composites has driven flexibility and miniaturization of the devices. Moreover, increased biomedical devices and structures based on these composites are on the horizon.

References

- Aditya, L., Mahlia, T., Rismanchi, B., *et al.*, 2017. A review on insulation materials for energy conservation in buildings. *Renewable and Sustainable Energy Reviews* 73, 1352–1365.
- Ajayan, P.M., Suhr, J., Koratkar, N., 2006. Utilizing interfaces in carbon nanotube reinforced polymer composites for structural damping. *Journal of Materials Science* 41, 7824–7829.
- Ali, A., Andriyana, A., 2020. Properties of multifunctional composite materials based on nanomaterials: A review. *RSC Advances* 10, 16390–16403.
- Babu, K., Rendén, G., Afriyie Mensah, R., *et al.*, 2020. A review on the flammability properties of carbon-based polymeric composites: State-of-the-art and future trends. *Polymers* 12, 1518.
- Bagwell, R.M., Mcmanaman, J.M., Wetherhold, R.C., 2006. Short shaped copper fibers in an epoxy matrix: Their role in a multifunctional composite. *Composites Science and Technology* 66, 522–530.
- Bai, Y., Jantunen, H., Juuti, J., 2018. Energy harvesting research: The road from single source to multisource. *Advanced Materials* 30, 1707271.
- Bar, M., Alagirusamy, R., Das, A., 2015. Flame retardant polymer composites. *Fibers and Polymers* 16, 705–717.
- Berardi, U., Iannace, G., 2015. Acoustic characterization of natural fibers for sound absorption applications. *Building and Environment* 94, 840–852.
- Biranje, S.S., Madiwale, P.V., Patankar, K.C., *et al.*, 2020. Cytotoxicity and hemostatic activity of chitosan/carrageenan composite wound healing dressing for traumatic hemorrhage. *Carbohydrate Polymers* 239, 116106.
- Cao, S., Zhu, W., Liu, T., 2020a. Bio-inspired self-healing polymer foams with bilayered capsule systems. *Composites Science and Technology* 195, 108189.
- Cao, Y., Zhang, J., Zhang, D., *et al.*, 2020b. A novel shape memory-assisted and thermo-induced self-healing boron nitride/epoxy composites based on Diels–Alder reaction. *Journal of Material Science* 55, 11325–11338.
- Cao, Z.-J., Liao, W., Wang, S.-X., Zhao, H.-B., Wang, Y.-Z., 2019. Polyurethane foams with functionalized graphene towards high fire-resistance, low smoke release, superior thermal insulation. *Chemical Engineering Journal* 361, 1245–1254.
- Cardoso, R.M., Silva, P.R.L., Lima, A.P., *et al.*, 2020. 3D-Printed graphene/poly(lactic acid) electrode for bioanalysis: Biosensing of glucose and simultaneous determination of uric acid and nitrite in biological fluids. *Sensors and Actuators B: Chemical* 307, 127621.
- Chandra, R.J., Shivamurthy, B., Kulkarni, S.D., Kumar, M.S., 2019. Hybrid polymer composites for EMI shielding application – A review. *Materials Research Express* 6, 082008.
- Chapman, C.A., Cuttaz, E.A., Goding, J.A., Green, R.A., 2020. Actively controlled local drug delivery using conductive polymer-based devices. *Applied Physics Letters* 116, 010501.
- Charles, A.D., Rider, A.N., Brown, S.A., Wang, C.H., 2020. Multifunctional magneto-polymer matrix composites for electromagnetic interference suppression, sensors and actuators. *Progress in Materials Science*. 100705.
- Chatterjee, S., Pandey, K., 2003. Thermoelectric cold-chain chests for storing/transporting vaccines in remote regions. *Applied energy* 76, 415–433.
- Chen, J., Zhu, Y., Huang, J., *et al.*, 2020. Advances in responsively conductive polymer composites and sensing applications. *Polymer Reviews*. 1–37.
- Christodoulou, L., Venables, J.D., 2003. Multifunctional material systems: The first generation. *JOM* 55, 39–45.
- Chuang, Y.-C., Li, T.-T., Huang, C.-H., *et al.*, 2016. Protective rigid fiber-reinforced polyurethane foam composite boards: Sound absorption, drop-weight impact and mechanical properties. *Fibers and Polymers* 17, 2116–2123.
- Chung, D., 2001. Materials for vibration damping. *Journal of Materials Science* 36, 5733–5737.
- Correia, D.M., Fernandes, L.C., Martins, P.M., *et al.*, 2020. Ionic liquid–polymer composites: A new platform for multifunctional applications. *Advanced Functional Materials*. 1909736.
- Curtis, P.T., 1996. Multifunctional polymer composites. *Advanced Performance Materials* 3, 279–293.
- Dan, L., Elias, A.L., 2020. Flexible and stretchable temperature sensors fabricated using solution-processable conductive polymer composites. *Advanced Healthcare Materials* 9, 2000380.
- Dathathri, E., Lal, S., Mittal, M., Thakur, G., De, S., 2020. Fabrication of low-cost composite polymer-based micro needle patch for transdermal drug delivery. *Applied Nanoscience* 10, 371–377.
- Du, W., Jin, Y., Lai, S., *et al.*, 2020. Multifunctional light-responsive graphene-based polyurethane composites with shape memory, self-healing, and flame retardancy properties. *Composites Part A: Applied Science and Manufacturing* 128, 105686.
- Ersoy, O., 2020. The effect of dispersion quality of fillers on soundproofing properties of acrylonitrile butadiene styrene/dense filler composites: Barite vs magnetite. *Polymer Composites* 41, 1045–1052.
- Eslahi, N., Mahmoodi, A., Mahmoudi, N., Zandi, N., Simchi, A., 2020. Processing and properties of nanofibrous bacterial cellulose-containing polymer composites: A review of recent advances for biomedical applications. *Polymer Reviews* 60, 144–170.
- Fan, W., Zhang, X., Zhang, Y., Zhang, Y., Liu, T., 2019. Lightweight, strong, and super-thermal insulating polyimide composite aerogels under high temperature. *Composites Science and Technology* 173, 47–52.
- Florea, I., Manea, D.L., 2019. Analysis of thermal insulation building materials based on natural fibers. *Procedia Manufacturing* 32, 230–235.
- Fràleoni-Morgera, A., Chhikara, M., 2019. Polymer-based nano-composites for thermal insulation. *Advanced Engineering Materials* 21, 1801162.
- Gandara-Loe, J., Souza, B.E., Missyul, A., *et al.*, 2020. MOF-based polymeric nanocomposite films as potential materials for drug delivery devices in ocular therapeutics. *ACS Applied Materials & Interfaces* 12, 30189–30197.
- Gao, D., Wen, X., Guan, Y., *et al.*, 2020. Flame retardant effect and mechanism of nanosized NiO as synergist in PLA/APP/CSI-MCA composites. *Composites Communications* 17, 170–176.
- Gariya, N., Prasad, B., Kumar, P., 2020. FEM based analysis of soft polymer composites with crack. *Materials Today: Proceedings* 28, 2426–2430.
- Goines, L., Hagler, L., 2007. Noise pollution: A modern plague. *Southern Medical Journal* 100, 287–294.
- Gokulkumar, S., Thyla, P.R., Prabhu, L., Sathish, S., 2019. Characterization and comparative analysis on mechanical and acoustical properties of *Camellia sinensis*/Ananas comosus/glass fiber hybrid polymer composites. *Journal of Natural Fibers*. 1–17.
- Gonçalves, S.S.L., Rudnitskaya, A., Sales, A.J., Costa, L.M.C., Evtuguin, D.V., 2020. Nanocomposite polymeric materials based on eucalyptus Lignoblast® kraft lignin for liquid sensing applications. *Materials* 13, 1637.
- Gou, L., Xiang, M., Ni, X., 2020. Development of wound therapy in nursing care of infants by using injectable gelatin-cellulose composite hydrogel incorporated with silver nanoparticles. *Materials Letters* 277, 128340.
- Groo, L., Steinke, K., Inman, D.J., Sodano, H.A., 2019. Vibration damping mechanism of fiber-reinforced composites with integrated piezoelectric nanowires. *ACS Applied Materials & Interfaces* 11, 47373–47381.
- Guo, Y., Ruan, K., Shi, X., Yang, X., Gu, J., 2020. Factors affecting thermal conductivities of the polymers and polymer composites: A review. *Composites Science and Technology*. 108134.

- Hadavi Moghadam, B., Hasanzadeh, M., Simchi, A., 2020. Self-powered wearable piezoelectric sensors based on polymer nanofiber-metal-organic framework nanoparticle composites for arterial pulse monitoring. *ACS Applied Nano Materials*.
- Hia, I.L., Vahedi, V., Pasbakhsh, P., 2016. Self-healing polymer composites: Prospects, challenges, and applications. *Polymer Reviews* 56, 225–261.
- Jaspal, D., Malviya, A., 2020. Composites for wastewater purification: A review. *Chemosphere* 246, 125788.
- Javadi, A., Afzal, A., 2018. Carbon fiber reinforced modified bisphenol-a diglycidylether epoxy composites for flame retardant applications. *Materials Research Express* 5, 065703.
- Jayaramudu, T., Varaprasad, K., Reddy, K.K., *et al.*, 2020. Chitosan-pluronic based Cu nanocomposite hydrogels for prototype antimicrobial applications. *International journal of biological macromolecules* 143, 825–832.
- Johns, A., Qian, J., Carolan, M.E., *et al.*, 2020. Functionalized electrospun polymer nanofibers for treatment of water contaminated with uranium. *Environmental Science: Water Research & Technology* 6, 622–634.
- Jony, B., Roy, S., Mulani, S.B., 2020. Fracture resistance of in-situ healed CFRP composite using thermoplastic healants. *Materials Today Communications* 24, 101067.
- Jony, B., Thapa, M., Mulani, S.B., Roy, S., 2019. Repeatable self-healing of thermosetting fiber reinforced polymer composites with thermoplastic healant. *Smart Materials and Structures* 28, 025037.
- Joy, A., Varughese, S., Kanjarla, A.K., Sankaran, S., Haridoss, P., 2020. Effect of the structure and morphology of carbon nanotubes on the vibration damping characteristics of polymer-based composites. *Nanoscale Advances* 2, 1228–1235.
- Kang, Y., Zhang, Y.-H., Sun, P.-P., *et al.*, 2020. Bimetallic coordination polymer composites: A new choice of electrode materials for lithium ion batteries. *Solid State Ionics* 350, 115310.
- Karim, M.R., Alam, M., Ajiaz, M., *et al.*, 2020. The fabrication of a chemical sensor with PANI-TiO₂ nanocomposites. *RSC Advances* 10, 12224–12233.
- Kim, M.S., Yan, J., Joo, K.H., *et al.*, 2013. Synergistic effects of carbon nanotubes and exfoliated graphite nanoplatelets for electromagnetic interference shielding and soundproofing. *Journal of Applied Polymer Science* 130, 3947–3951.
- Kim, N., Lienemann, S., Petsagkourakis, I., *et al.*, 2020. Elastic conducting polymer composites in thermoelectric modules. *Nature Communications* 11, 1424.
- Kolya, H., Kang, C.W., 2020. High acoustic absorption properties of hackberry compared to nine different hardwood species: A novel finding for acoustical engineers. *Applied Acoustics* 169, 107475.
- Kumar, A., Claire, S., Khanna, J., *et al.*, 2020. Experimental study to measure the sound transmission loss and equivalent continuous sound pressure level of composite material for various disturbances. *Materials Today: Proceedings* 27, 2782–2786.
- Li, M., Wang, M., Hou, X., *et al.*, 2020a. Highly thermal conductive and electrical insulating polymer composites with boron nitride. *Composites Part B: Engineering* 184, 107746.
- Li, S., Yi, J., Yu, X., Wang, Z., Wang, L., 2020b. Preparation and characterization of pullulan derivative/chitosan composite film for potential antimicrobial applications. *International Journal of Biological Macromolecules* 148, 258–264.
- Liu, J., Liu, G., Xu, J., *et al.*, 2020. Graphene/polymer hybrid fiber with enhanced fracture elongation for thermoelectric energy harvesting. *ACS Applied Energy Materials* 3, 6165–6171.
- Lu, L., Yang, B., Liu, J., 2020. Flexible multifunctional graphite nanosheet/electrospun-polyamide 66 nanocomposite sensor for ECG, strain, temperature and gas measurements. *Chemical Engineering Journal* 400, 125928.
- Luo, X., Shen, J., Ma, Y., *et al.*, 2020. Robust, sustainable cellulose composite aerogels with outstanding flame retardancy and thermal insulation. *Carbohydrate Polymers* 230, 115623.
- Ma, Y., Zhang, Y., Liu, J., *et al.*, 2020. GO-modified double-walled polyurea microcapsules/epoxy composites for marine anticorrosive self-healing coating. *Materials & Design* 189, 108547.
- Mallick, S., Ahmad, Z., Qadir, K.W., *et al.*, 2020. Effect of BaTiO₃ on the sensing properties of PVDF composite-based capacitive humidity sensors. *Ceramics International* 46, 2949–2953.
- Marques, B., António, J., Almeida, J., *et al.*, 2020a. Vibro-acoustic behaviour of polymer-based composite materials produced with rice husk and recycled rubber granules. *Construction and Building Materials* 264, 120221.
- Marques, B., Tadeu, A., António, J., Almeida, J., De Brito, J., 2020b. Mechanical, thermal and acoustic behaviour of polymer-based composite materials produced with rice husk and expanded cork by-products. *Construction and Building Materials* 239, 117851.
- Menazea, A.A., Eid, M.M., Ahmed, M.K., 2020. Synthesis, characterization, and evaluation of antimicrobial activity of novel chitosan/tigecycline composite. *International Journal of Biological Macromolecules* 147, 194–199.
- Milazzo, M., Gallone, G., Marcello, E., *et al.*, 2020. Biodegradable polymeric micro/nano-structures with intrinsic antifouling/antimicrobial properties: Relevance in damaged skin and other biomedical applications. *Journal of Functional Biomaterials* 11, 60.
- Modi, A., Bellare, J., 2020. Efficient removal of 2,4-dichlorophenol from contaminated water and alleviation of membrane fouling by high flux polysulfone-iron oxide/graphene oxide composite hollow fiber membranes. *Journal of Water Process Engineering* 33, 101113.
- Muthusankar, E., Wabaidur, S.M., Alothman, Z.A., *et al.*, 2020. Fabrication of amperometric sensor for glucose detection based on phosphotungstic acid-assisted PDPA/ZnO nanohybrid composite. *Ionics*. 1–9.
- Nie, J., Xie, H., Zhang, M., *et al.*, 2020. Effective and facile fabrication of MOFs/cellulose composite paper for air hazards removal by virtue of in situ synthesis of MOFs/chitosan hydrogel. *Carbohydrate Polymers* 250, 116955.
- Ohayon-Lavi, A., Buzaglo, M., Ligati, S., *et al.*, 2020. Compression-enhanced thermal conductivity of carbon loaded polymer composites. *Carbon* 163, 333–340.
- Osterrieth, J.W., Fairen-Jimenez, D., 2020. Metal-organic framework composites for theragnostics and drug delivery applications. *Biotechnology Journal*. 2000005.
- Ouyang, C., Zhao, C., Li, W., *et al.*, 2020. Super-tough, self-healing polyurethane based on Diels-Alder bonds and dynamic zinc-ligand interactions. *Macromolecular Materials and Engineering*. 2000089.
- Pan, Y.-T., Zhang, Z., Yang, R., 2020. The rise of MOFs and their derivatives for flame retardant polymeric materials: A critical review. *Composites Part B: Engineering*. 108265.
- Pawar, D., Rao, C.N., Cao, P., 2020. Smart Polymer-Based Chemical Sensors. *Actuators: Fundamentals, Principles, Materials and Applications*. 75–138.
- Prabhu, L., Krishnaraj, V., Gokulkumar, S., Sathish, S., Ramesh, M., 2019. Mechanical, chemical and acoustical behavior of sisal – Tea waste – Glass fiber reinforced epoxy based hybrid polymer composites. *Materials Today: Proceedings* 16, 653–660.
- Prajapati, D.G., Kandasubramanian, B., 2019. Progress in the development of intrinsically conducting polymer composites as biosensors. *Macromolecular Chemistry and Physics* 220, 1800561.
- Qian, Y., Zhou, Y., Li, L., *et al.*, 2020. Facile preparation of active lignin capsules for developing self-healing and UV-blocking polyurea coatings. *Progress in Organic Coatings* 138, 105354.
- Rafiee, M., Nitzsche, F., Labrosse, M.R., 2019. Processing, manufacturing, and characterization of vibration damping in epoxy composites modified with graphene nanoplatelets. *Polymer Composites* 40, 3914–3922.
- Rahmani, H., Mahmoudi Najafi, S.H., Ashori, A., *et al.*, 2020. Preparation of chitosan-based composites with urethane cross linkage and evaluation of their properties for using as wound healing dressing. *Carbohydrate Polymers* 230, 115606.
- Sahu, P., Bhowmick, A.K., 2020. Sustainable water responsive mechanically adaptive and self-healable polymer composites derived from biomass. *Processes* 8, 726.
- Samuel, J.B., Jaisingh, S.J., Sivakumar, K., Mayakannan, A., Arunprakash, V., 2020. Visco-elastic, thermal, antimicrobial and dielectric behaviour of areca fibre-reinforced nano-silica and neem oil-toughened epoxy resin bio composite. *Silicon*. 1–10.
- Senzaki, M., Kadoya, T., Francis, C.D., 2020. Direct and indirect effects of noise pollution alter biological communities in and near noise-exposed environments. *Proceedings of the Royal Society B* 287, 20200176.

- Seshadri, A., Vedula, G., Naguib, H.E., 2020. Scalable sensing of hydrocarbon pollutants using soluble chemiresistive polymer composites. *Materials Chemistry and Physics* 239, 122119.
- Shahidzadeh, M., Varkaneh, Z.K., Ramezanzadeh, B., Pedram, M.Z., Yarmohammadi, M., 2020. Self-healing dual cured polyurethane elastomeric coatings prepared by orthogonal reactions. *Progress in Organic Coatings* 140, 105503.
- Sharma, S., Virk, K., Sharma, K., *et al.*, 2020. Preparation of gum acacia-poly(acrylamide-IPN-acrylic acid) based nanocomposite hydrogels via polymerization methods for antimicrobial applications. *Journal of Molecular Structure* 1215, 128298.
- Shin, P.-S., Kim, J.-H., Devries, K.L., Park, J.-M., 2020. Manufacturing and qualitative properties of glass fiber/epoxy composite boards with added air bubbles for airborne and solid-borne sound insulation. *Composites Science and Technology*. 108166.
- Song, S., Wang, J., Liu, C., Wang, J., Zhang, Y., 2019. A facile route to fabricate thermally conductive and electrically insulating polymer composites with 3D interconnected graphene at an ultralow filler loading. *Nanoscale* 11, 15234–15244.
- Stansfeld, S.A., Matheson, M.P., 2003. Noise pollution: Non-auditory effects on health. *British Medical Bulletin* 68, 243–257.
- Takagi, H., 2019. Review of functional properties of natural fiber-reinforced polymer composites: Thermal insulation, biodegradation and vibration damping properties. *Advanced Composite Materials* 28, 525–543.
- Tang, L., He, M., Na, X., *et al.*, 2019. Functionalized glass fibers cloth/spherical BN fillers/epoxy laminated composites with excellent thermal conductivities and electrical insulation properties. *Composites Communications* 16, 5–10.
- Tang, X., Yan, X., 2020. A review on the damping properties of fiber reinforced polymer composites. *Journal of Industrial Textiles* 49, 693–721.
- Tiuc, A.E., Nemeş, O., Vermeşan, H., Toma, A.C., 2019. New sound absorbent composite materials based on sawdust and polyurethane foam. *Composites Part B: Engineering* 165, 120–130.
- Tiwari, S., Purabgola, A., Kandasubramanian, B., 2020. Functionalised graphene as flexible electrodes for polymer photovoltaics. *Journal of Alloys and Compounds* 825, 153954.
- Trask, R., Williams, H., Bond, I., 2007. Self-healing polymer composites: Mimicking nature to enhance performance. *Bioinspiration & Biomimetics* 2, P1.
- Tshikovhi, A., Mishra, S.B., Mishra, A.K., 2020. Nanocellulose-based composites for the removal of contaminants from wastewater. *International Journal of Biological Macromolecules* 152, 616–632.
- Vatankhah, Z., Dehghani, E., Salami-Kalajahi, M., Roghani-Mamaqani, H., 2020. Seed's morphology-induced core-shell composite particles by seeded emulsion polymerization for drug delivery. *Colloids and Surfaces B: Biointerfaces* 191, 111008.
- Verma, S., Singh, H., 2019. Vacuum insulation in cold chain equipment: A review. *Energy Procedia* 161, 232–241.
- Wanasinghe, D., Aslani, F., Ma, G., Habibi, D., 2020. Review of polymer composites with diverse nanofillers for electromagnetic interference shielding. *Nanomaterials* 10, 541.
- Wang, F., Wang, B., Li, X., *et al.*, 2020a. Antimicrobial cationic acrylate-based hybrid coatings against microorganism contamination. *Progress in Organic Coatings* 142, 105576.
- Wang, X., Wu, P., 2019. One-step photo-mediated grafting of poly (methyl methacrylate) onto fluorinated carbon nanotube for the enhanced thermal conductive property of polymer composites. *Chemical Engineering Journal* 369, 272–279.
- Wang, Y., Jiang, D., Zhang, L., *et al.*, 2019. Hydrogen bonding derived self-healing polymer composites reinforced with amidation carbon fibers. *Nanotechnology* 31, 025704.
- Wang, Y., Li, Y., Wang, L., *et al.*, 2020b. Gradient-layered polymer nanocomposites with significantly improved insulation performance for dielectric energy storage. *Energy Storage Materials* 24, 626–634.
- Wu, P., Liu, L., Wu, Z., 2020. Synthesis of Diels-Alder reaction-based remendable epoxy matrix and corresponding self-healing efficiency to fibrous composites. *Macromolecular Materials and Engineering*. 2000359.
- Xiang, D., Zhang, Z., Han, Z., *et al.*, 2020. Effects of non-covalent interactions on the properties of 3D printed flexible piezoresistive strain sensors of conductive polymer composites. *Composite Interfaces*. 1–15.
- Xu, Z., Jin, C., Cabe, A., *et al.*, 2020. Flexible energy harvester on a pacemaker lead using multibeam piezoelectric composite thin films. *Acs Applied Materials & Interfaces* 12, 34170–34179.
- Xue, B., Xie, L., Bao, Y., Zhang, J., 2019. Multilayered epoxy/glass fiber felt composites with excellently acoustical and thermal insulation properties. *Journal of applied polymer science* 136, 46935.
- Xue, Y., Li, C., Liu, J., *et al.*, 2020. Fabrication and characterization of hierarchical microcapsules with multi-storage cells for repeatable self-healing. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 603, 125201.
- Yuan, D., Guo, H., Ke, K., Manas-Zloczower, I., 2020. Recyclable conductive epoxy composites with segregated filler network structure for EMI shielding and strain sensing. *Composites Part A: Applied Science and Manufacturing* 132, 105837.
- Yuan, H., Wang, Y., Li, T., *et al.*, 2019. Fabrication of thermally conductive and electrically insulating polymer composites with isotropic thermal conductivity by constructing a three-dimensional interconnected network. *Nanoscale* 11, 11360–11368.
- Zamal, H.H., Barba, D., Aïssa, B., Haddad, E., Rosei, F., 2020. Recovery of electro-mechanical properties inside self-healing composites through microencapsulation of carbon nanotubes. *Scientific Reports* 10, 2973.
- Zhang, L.-P., Liu, Z., Zhou, X.-L., *et al.*, 2020a. Novel composite membranes for simultaneous catalytic degradation of organic contaminants and adsorption of heavy metal ions. *Separation and Purification Technology* 237, 116364.
- Zhang, M., Cui, J., Lu, T., *et al.*, 2021. Robust, functionalized reduced graphene-based nanofibrous membrane for contaminated water purification. *Chemical Engineering Journal* 404, 126347.
- Zhang, W., Cao, S., Wu, Z., *et al.*, 2020b. High-performance gas sensor of polyaniline/carbon nanotube composites promoted by interface engineering. *Sensors* 20, 149.
- Zhang, W., Zhang, X., Wu, Z., *et al.*, 2020c. Mechanical, electromagnetic shielding and gas sensing properties of flexible cotton fiber/polyaniline composites. *Composites Science and Technology* 188, 107966.
- Zhang, X., Wu, K., Liu, Y., *et al.*, 2019. Preparation of highly thermally conductive but electrically insulating composites by constructing a segregated double network in polymer composites. *Composites Science and Technology* 175, 135–142.
- Zhao, J., Wang, G., Wang, C., Park, C.B., 2020. Ultra-lightweight, super thermal-insulation and strong PP/CNT microcellular foams. *Composites Science and Technology* 191, 108084.
- Zhou, X., Zhang, X., Zhao, H., Krishnan, B.P., Cui, J., 2020. Self-healable and recyclable tactile force sensors with post-tunable sensitivity. *Advanced functional materials*. 2003533.
- Zhou, X.Q., Yu, D.Y., Shao, X.Y., Zhang, S.Q., Wang, S., 2016. Research and applications of viscoelastic vibration damping materials: A review. *Composite Structures* 136, 460–480.
- Zhou, Y., Wang, Q., 2020. Advanced polymer dielectrics for high temperature capacitive energy storage. *Journal of Applied Physics* 127, 240902.
- Zou, D., Huang, X., Zhu, Y., Chen, J., Jiang, P., 2019. Boron nitride nanosheets endow the traditional dielectric polymer composites with advanced thermal management capability. *Composites Science and Technology* 177, 88–95.

Polymer Matrix Composite Materials for Aerospace Applications

Subramani Devaraju, Vignan's Foundation for Science, Technology and Research, Guntur, India

Muthukaruppan Alagar, PSG Institute of Technology and Applied Research, Coimbatore, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

Composite materials consist of two or more diverse components that are chemically or physically networked together. Each of the constituents reveals their distinctive typical properties. The composites comprise of two phases specifically polymer matrix preferably organic phase and reinforcement predominantly inorganic nature. The polymer segments are the continuous phase and fillers are either discontinuous or continuous according to their dimension and length scale. The reinforcement contributes to the asset of the composites and the matrix makes the fillers integral with robust and efficient adhesion. The composites are deliberated as vibrant materials in the contemporary world, owing to their collective properties, viz., light weight, high strength, good stiffness, high thermal stability, low moisture and weather absorption, resist against fire/flame and corrosion, and decent dielectric behavior, which are not conceivable to derive from the single constituents. They are extensively used in the production/fabrication of aerospace structures, packaging of medical and electronic equipments, space vehicle, construction, and etc (Thomas *et al.*, 2012; Cantor *et al.*, 2015; Njuguna, 2016; Mouritz, 2012; Njuguna and Pielichowski, 2003; Toldy *et al.*, 2011; Wang *et al.*, 2011; Mangalgiri, 1999; Devaraju and Alagar, 2018; Quilter, 2001; Ratna and Karger-Kocsis, 2008; Alimuzzaman, 2014; Taj *et al.*, 2007; Liu *et al.*, 2014; Williams *et al.*, 2007; Nurhaniza *et al.*, 2010; Brown, 2014; Toozandehjani *et al.*, 2018).

Polymer matrix composites are one of the most cost inexpensive and advanced composite materials used for extensive range of engineering applications. These composites comprise of either thermosetting or thermoplastic resinous binder reinforced with natural or synthetic materials in the form of fibers, flakes, or particles. They provide an avenue to obtain the improved and optimum properties required for indented applications such as good stiffness and strength, and good corrosion resistance. Polymeric materials have number of benefits over the traditional materials those have been applicable in various aerospace structures (Ratna and Karger-Kocsis, 2008). Owing to their amenable industrial design advantages, including precise strength with a lower weight (weight reduction over the 40%). The other benefits including rapid process for production series, capacity to encounter rigorous dimensional stability, excellent fracture and fatigue resistance, and minor coefficient thermal expansion behaviors when compared to ceramics and metals (Liu *et al.*, 2014). There are numerous potentials for developing composites using diverse combinations of fillers, fibrous additives, and polymer matrices (Alimuzzaman, 2014). These materials play major in advanced composites sector because of their cost competitive, good strength, easy fabrication process, and flexibility in the design (Taj *et al.*, 2007).

Current aerospace sectors are more focused on substituting the secondary structures with fiber based polymer matrix composites, where the fiber used as either glass, Kevlar, carbon, or mixture of these materials (Williams *et al.*, 2007). The necessity for high performance and competence to design material features to encounter definite desires has made the polymer composites a major choice for several aerospace applications. Such materials able to be custom-made to provide good strength combined with reasonably lesser weight, good chemical and corrosion resistance, and to offer longer durability under supreme severe environmental conditions.

Composite Materials in Aerospace Structure

Metals like steel, aluminum, and titanium are utilized to reign extreme in the aerospace applications, accounts about 70% of the aircraft. Yet as hassles for reduction in weight and to improve fuel competence, metals are trailing ground to some of the versatile thermoplastic polymers and composites. The properties of newly developed materials are expected to replace some of the conventional materials in construction of the latest generation of modern aircraft and needs to be assessed their impact on aerospace manufacturing (Mangalgiri, 1999; Toozandehjani *et al.*, 2018).

Until recently, metals are most commonly utilized in the fabrication of aerospace components, conversely, improvements in materials science, specifically in composites field, endorsed the progress of favorable materials for aerospace applications. The huge increase in the costs of aviation turbine fuel (ATF) have ensued in larger request for lesser weight materials in aerospace sectors (Waheedullah Ghori *et al.*, 2018). In the aerospace sector, about 50% of the working cost is exploited for consumption of fuel.

Polymeric composites have key benefits over the traditional metallic materials those are used in diverse aerospace structures. Recent military aircraft have reduced their weight up to 30% with the use of polymer matrix composites. The polymer matrix composites establish ~80% of current launch transportation for satellites, consist of numerous vibrant satellite constituents such as the equipment panels, honey comb assemblies, cylinder sustenance structures, substrates for solar array, antennas, and etc. 30 tons of graphite filled epoxy composites are involved in the space vehicle's (Mouritz, 2012; Waheedullah Ghori *et al.*, 2018). Another significant solicitation of polymers as a bonding agent for linking aerospace constituents. It's probable to acquire good strength, durable links by polymer adhesives. A tinny layer of polymer adhesive is applied to link together with the fiber based

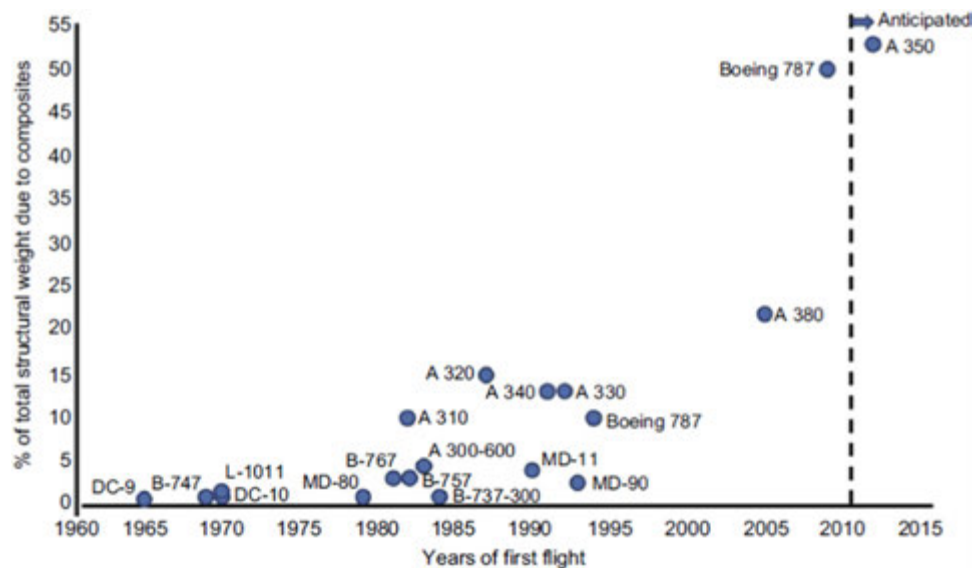


Fig. 1 Usage of polymer matrix composites in aerospace sectors over the years Copyright 2016. Reproduced with permission from In: Rana, S., Figueiro, R. (Eds.), 2016. *Advanced Composite Materials for Aerospace Engineering Processing, Properties and Applications*. Woodhead Publishing Series in Composites Science and Engineering. Elsevier, from Elsevier.

polymer composite and aluminum sheets, that yield the fiber reinforced metal laminate termed as GLARE (Glass laminate aluminum reinforced epoxy), which is utilized to fabricate the fuselage of Airbus 380. The usage of elastomer based materials is generally narrowed to nonstructural aircraft components that need good elasticity and flexibility, including gaskets and seal. Though, polymers with fiber reinforcements or metal sometimes struggle for having more viscosities, higher fabrication temperature and pressure, meager resistance to creep, and etc. Also they look glitches associated to larger weight, aggregation, inadequate stress dissemination, and other aspects (Cantor *et al.*, 2015; Waheedullah Ghorri *et al.*, 2018).

Composites are developed by comprising of two or more constituents, in order to exploit the beneficial features of individual component (Devaraju and Alagar, 2018). Composite materials are most widely used in the aerospace sector in both primary and secondary components, such as engine nacelles, antenna dishes, radomes, vertical and horizontal stabilizers, aircraft wings, center wing boxes, pressure bulk heads, doors of landing gear, engine cowlings, tall cones, floor beams, flap track panels, and etc. The progress of polymer matrix composites usage in viable aircrafts is presented in Fig. 1. The Boeing 777 is a twin-engine jet airliner launched in 2000 with capability of over the 300 travelers, used 11% of polymer composite materials (Table 1). The Boeing 787 Dreamliner, launched in the year 2007, they used over the 50% polymer composites (nearly 3.2 tons of carbon fiber reinforced polymer composites). In recent times, fiber reinforced polymer composites (FRPs), developed with various types of matrices (e.g., metal, ceramic and polymer, etc.), with fiber materials, are attain remarkable consideration in aerospace applications. In today's aerospace sectors, the use of composite materials has enlarged over the 50% (Rana and Figueiro, 2016). For example, the airbus A350 XWB fabricated using carbon-reinforced polymeric composites over 50%, while its colleague, the Boeing 787, also used ~50% polymer matrix composites (Fig. 2) (Brown, 2014). Remarkably, this tendency is not restricted to Airbus and Boeing; other concerns including BAE Systems, Bombardier, GE Aviation, Raytheon, and Lockheed Martin have also tended into use of polymeric matrix composites in their aerospace structures. These improvements in materials are ambitious by numerous factors.

Some of the significant necessities for aerospace materials are specified below.

- (1) High strength
- (2) Light weight
- (3) High damage tolerance
- (4) Good fracture resistance

Advanced Composite Component Materials in Aerospace Structure

Polymeric matrix composites have been several uses in the aerospace sectors. Every so often utilizations do come nearby where the price is secondary anxiety, as usually advanced polymer matrix composites for definite applications are very costly. Such applications including crew gear and cockpit, space optical devices; heat shrinkage pipes, substrates for solar array; high and temperature flare housing, nozzles and shrouds; moldings appliance; durable space mirrors; detectors with high-precision; multifunctional satellite, bus structures; interiors of aircraft; and structural space components (Liu *et al.*, 2014; Lubin, 2013). Advances in polymeric composites will endure to combine with new forthcoming technologies satisfying definite aerospace desires

Table 1 Usage of polymer composites in Boeing aerospace structures

Materials %	Boeing 787 dreamliner	Boeing 777
Launched in	2007	2000
FRPs	50%	11%
Aluminum	20%	70%
Titanium	15%	7%
Steel	10%	11%
Others	5%	1%

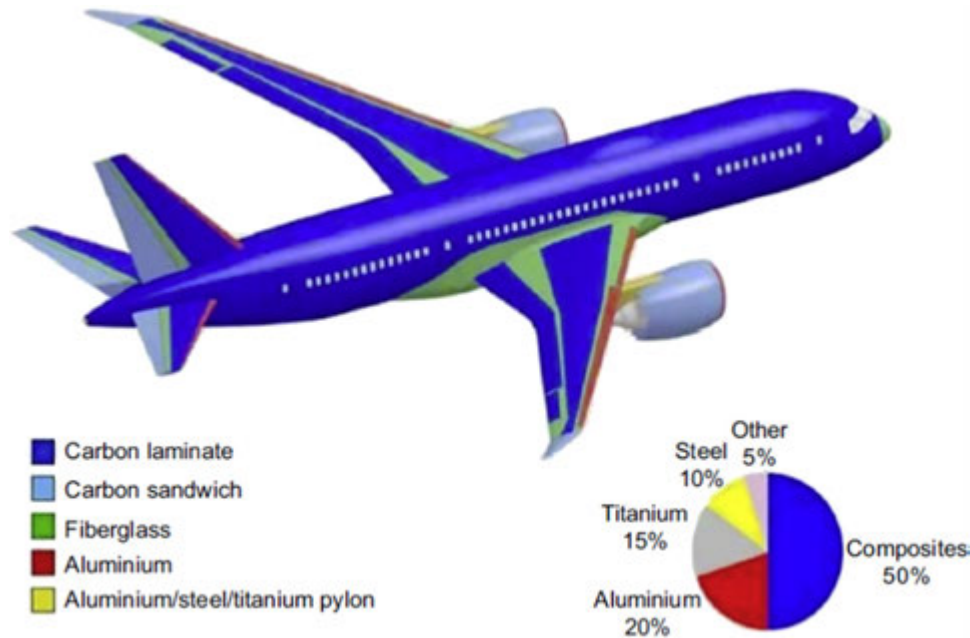


Fig. 2 Usage of polymer composites in Boeing 787. Copyright 2016. Reproduced with permission from In: Rana, S., Figueiro, R. (Eds.), 2016. Advanced Composite Materials for Aerospace Engineering Processing, Properties and Applications. Woodhead Publishing Series in Composites Science and Engineering. Elsevier, from Elsevier.

(Njuguna and Pielichowski, 2003). Robust engineering technology for polymeric matrix composites will enrich the role of polymers as a facilitating technology, by such features including design optimization, electronics, bio mimetics, reliability and control technology constructing key influences. The outcomes of these expertise will lead to advanced polymer composites with enormous applications including ultra-light aerospace structures or thin films, shape memory polymer for spacecraft, polymers fir electro-active, electro-chromic, and thermo-optical applications (Quilter, 2001; Mouritz *et al.*, 1999; Yan *et al.*, 2008).

The prime emphasis in the progress of an advanced composites have been to discourse their susceptibility to impact destruction (Yadav *et al.*, 2020). The orthotropic behavior of polymer composites consequences in a reasonably low thickness strength which is over and over again alleviated by creating damage lenient designs for structural constituents. Williams *et al.* (2007) examined the influence of the hollow glass fiber (HGF) embedded on the carbon fiber filled epoxy (CFRP) on mechanical behavior, and the healing effectiveness of the laminates after exposed to impact. Samples were confirmed in the damaged, undamaged, and healed conditions with a conventional epoxy healing agent. Rana and Figueiro (Rana and Figueiro, 2016) have categorized the advanced matrix composite in several application based on necessities, structure and fabrication methods as displayed in Table 2.

The aerospace sectors is expected to be the key benefactor of the development of polymer composites as new technology progresses. Frequently, the aerospace application wanted high performance materials with good durability for prolonged life time in sever and volatile climatic circumstances that conventional composite materials struggle to encounter (Waheedullah Ghori *et al.*, 2018).

The Aerospace Structures and Features

The essential necessities of an aerospace assembly and their consequence on the strategy of the structure are depicted in Table 3. Furthermore, the assembly has to full fill the necessities of fuel sealing and deliver admittance for tranquil maintenance of the

Table 2 Advanced composite materials and their properties

Advanced composites	Properties	Materials
Laminated composites	Improved fracture toughness, Enhanced impact properties, Damage tolerance,	E-glass, para aramid fiber, carbon fiber, and other textile based system in various structural design
Sandwich composites	Light weight; Cost effective; Good bending stiffness; Thermal and noise insulation; Damping vibration (Velosa et al., 2012)	Polymer Matrices: Vinyl ester, unsaturated polyester, Epoxy, polyether etherketone (PEEK), polyetherimide (PEI), polycarbonate (PC). Filler reinforcements: Glass fiber (E & S), high modulus carbon, high strength carbon, aramid and Boron fiber.
Braided composites	High shear strength and stiffness; High fracture toughness; High transverse strength and modulus; Fatigue life and damage tolerance and; Notch insensitivity (Rana et al., 2015)	Polymer Matrices: Polyester, Epoxy, PEEK, nylon 6,6, and polypropylene (PP) Filler Reinforcements: Aramid Carbon T300 (Barbero, 2017), Carbon T600 (Carey et al., 2016)
Auxetic composites	Good fracture toughness; Good shear modulus; Good damping resistance; Synclastic curvature; Superior crack growth resistance; High energy absorption ability (Subramani et al., 2014)	Polymer Matrices: Epoxy, polytetrafluoroethylene (PTFE), polyurethane (PU), ultra-high-molecular-weight polyethylene (UHDPE). Reinforcements: Glass and carbon fiber
Ceramic matrix composites	Light weight; High strength; Good fracture toughness; Resistance to catastrophic failure; Good oxidation resistance; Low thermal expansion; Capacity to survive at higher temperature (Hull and Clyne, 1996)	Boron/glass/oxide fibers, SiC HP, aluminosilicate 1720, mullite, Si ₃ N ₄ HP, and glass ceramics nonmachinable 9606,
Metal-matrix composites	High transverse stiffness and strength; High fracture toughness and ductility; High thermal/fire resistance; Good thermal and electrical and conductivities; Good resistance to moisture absorption; Good radiation protection (Clyne and Withers, 1995)	Glass/boron fibers, magnesium, aluminum, and titanium
Nanocomposites	Higher surface area and good interface, Smaller defects, Low volume fraction necessary for the enhancement of properties (Thostenson et al., 2005a)	Phenolic, Epoxy, polyimide (PI), bismaleimide (BMI), PEK, PEKK, elastomers, single/multi-walled carbon nanotube, graphene, etc.

equipments. Traveler carriage wants fire, smoke and toxicity (FST) as per safety criterions to be tailed and these laid distinct demands of crash-worthiness and fire resistant on the constituents and design used. For space craft vehicles the space surroundings including radiation, vacuum, and thermal cycling have to be deliberated for specifically established materials for their resilience in operation. The key parameters involved in the development of scientific-technology related with aerospace applications are influence on the generation and fulfillment of the hassles embossed by aerospace civic has been simplified by computational and modeling tools in the manufacturing ([Mangalgiri, 1999](#)).

Use of Composites in Aerospace Structure

In order to meet the demands for aerospace structures are presented in [Table 3](#), it's essential to devour materials with a typical properties combinations ([Mangalgiri, 1999](#); [Kesarwani, 2017](#)). The use of polymer matrix composite materials has been inspired by such considerations. In precise, the advanced fiber filled polymer composites using aramid/carbon fibers delivers several features as given beneath:

- (1) Light-weight due to high strength and stiffness;
- (2) Corrosion and fatigue-resistance;
- (3) Competence for high-degree of optimization: adapting the directional strength and stiffness;
- (4) Ability to mold for larger shapes in short cycle time;
- (5) Worthy for thinner walled/generously curved construction;
- (6) Competence to withstand the alignment and dimensional stability in space surroundings;
- (7) Probability of lower dielectric loss in radar transparency;
- (8) Possibility of attaining the minimal radar cross section;
- (9) These composite materials also have certain intrinsic weaknesses;
- (10) Laminated construction with fragile interfaces: meager resistance to tensile loads;
- (11) Liability to impact-damage and robust possibility of interior damage going unnoticed;
- (12) Absorption of moisture and subsequent deterioration of elevated temperature performance;
- (13) Diversity of probable manufacturing shortcomings and inconsistency in the material properties.

Even after taking careful considerations of these limitations, the expected benefits are substantial and nearly all aerospace construction uses the sizable portion of polymer based composites.

Table 3 Features of aircraft structure

<i>Requirements</i>	<i>Applicability</i>	<i>Effect</i>
Light weight	All aerospace components	● Semi-monocoque construction 1. Stiffened structures or thinner walled box ● Using lower density materials: 1. Al-alloys 2. Wood 3. Composites ● High stiffness/weight and high strength /weight
Good reliability	All aerospace components	● Severe quality control ● Extensive analysis for consistent data ● Certification: Proof of design
Traveler safety	Traveler vehicles	● Using fire resistant materials ● Extensive analysis: Crash-worthiness ● Extensive fatigue testing
Durability fatigue and corrosion degradation: Vacuum radiation thermal	Aircraft spacecraft	Aluminum alloys don't have a fatigue limit. ● Prevention corrosion schemes ● Concerns of damage and safer life, extension of life ● Extensive analysis for necessary surroundings
Aerodynamic performance	Aircraft reusable spacecraft	● Tinny materials with extraordinary integrity ● Highly complex loading ● Thin bendable wings, control and surfaces 1. Dynamics 2. Distorted shape-aero elasticity ● Complex contoured shapes
Multi-role or functionality	● All aerospace components	1. Manufacturability: N/C machining; molding ● Capable design ● Use: composite materials with varying functional properties
Fly-by-wire	Aircrafts, generally for fighters and also some in traveler a/c	● Structure-control interactions 1. Aero-servo-elasticity ● Widespread use of computers/electronics
Stealth	Precise aerospace applications in military	1. Electromagnetic interference shielding ● Definite surface and shape of aircraft
All-weather operation	Air-craft	1. Stealth coatings. ● Lightning protection, resistance against erosion

Materials for Aerospace Composites

The material structures which have been deliberated beneficial in aerospace industry are based on emphasizing fibers and resin matrices given in [Tables 4](#) and [5](#), correspondingly. Utmost aerospace structures use prepregs as staring materials with autoclave molding as a common construction process. Filament winding is one of standard with similar to shell constituents including rocket motor casings for takeoff missiles and vehicles. For lower speed small aircraft constructed using glass fiber reinforced composites by either room temperature or oven curing. It's collective to utilize composites tooling where production degrees are moderate or small; though, where huge number of constituents are necessary, metallic traditional tooling is desired ([Mangalgiri, 1999](#); [Kesarwani, 2017](#)). Resin injection molding (RTM) also discovers use in distinctive components including radomes.

Table 4 Most commonly used polymeric matrices in aerospace applications

<i>Thermoset</i>				<i>Thermoplastics</i>
<i>Epoxies</i>	<i>Phenolics</i>	<i>Polyester</i>	<i>Polyimides</i>	<i>PPS, PEEK</i>
- Most popular resins used for aerospace. - Composite total usage of about 80% - Reasonably high temperature - Relatively costly	- Inexpensive - Easy to use - Low viscosity - High temperature usage - Very hard to obtain high quality composites	- Inexpensive - Easy to use - More popular at room temperature applications	- Applicable for high temperature applications $\sim 300^{\circ}\text{C}$ - Difficulty in fabrication process - Highly brittle in nature	- Good in damage tolerance - Difficulty in the fabrication process as high temperature $300\text{--}400^{\circ}\text{C}$ is necessary
- Minimal shrinkage (2%–3%); - No volatile release during polymerization (curing). - Can be cured in several methods giving diversities of structures and morphology with widespread range of properties	- High shrinkage - During polymerization release of volatiles - Good inherent thermal oxidation stability - Good resistance against fire and flame retardance - Brittle than epoxies	- More shrinkage (7%–8%) - Better chemical resistance properties - Broad range of properties (lower than epoxies). - Brittle in nature - Lower T_g - Difficulty to make prepregs - Less sensitive to moisture when compared to epoxies		Infinite storage life.
- High storage stability to prepare prepregs - Absorb moisture about 5%–6% result in swelling and degradation of composites at high temperature properties - Led to ultra violet degradation in long duration. - Density: 1.1–1.4 - Tensile strength: 40–85 MPa	- Lower storage stability and difficulty to make prepregs - Absorbs moisture though there is no substantial influence of moisture in operational service range - Density: 1.2–1.4 - Tensile strength: 35–60 MPa	- Density: 1.1–1.4 - Tensile strength: 40–85 MPa - Tensile modulus: 2.7 to 4.1 GPa		- Difficulty to make prepregs - Good resistance against moisture
Tensile modulus: 2.7–5.5 GPa	Tensile modulus: 2.7 to 4.1 GPa	Tensile modulus: 1–3–4.1 GPa		- Density: 1.3–1.4 - Tensile strength: 100 MPa - Tensile modulus: 3.5–4.4 GPa

Reinforcements for Aerospace Materials

Reinforcement (filler) materials incorporated in polymer composites are usually harder, stiffer and stronger, stiffer than the polymer matrix materials. Intrinsically, they performance as the main load resonant component than make up to 60%–70% of the volume of the composites (fiber volume portion). Utmost structural uses trust on continuous, tinny thickness, emphasizing fibers, as these afford a reasonably enormous fiber matrix interface region that consents for superior bonding and load transfer. A series of diverse fiber materials will be utilized to produce thermoset composite fragments, reliant on cost competitive and performance needs. Typical composite material systems used in aerospace applications depicted in [Table 6](#).

Glass fibers (GFs) are one of the widely utilized among all other synthetic fibers as it deliver excellent durability and strength, good thermal stability, impact resistance, chemical resistance, friction resistance, and wear resistant properties. Though, the machining of glass fiber incorporated polymers (GFRPs) is comparatively slow, challenging, and shows compact tool life whereas working on conformist machining systems ([Rajak et al., 2019](#); [Prakash, 2019](#)). Also GFs express the shortcoming of disposal after it uses ([Chalmers, 1991](#)). GFs are relatively inexpensive, have a diameter of 10–20 μm , and are extensively utilized in the automotive and marine applications. Moreover, GFs composites are establish on the secondary components of traveler aircraft, but fairly poor stiffness and strength has prohibited its use on primary components (load-bearing) in the larger aircraft structures, apart from being used as an insulating layer (electrically). One prominent exception is the utilize of GLARE on the top fuselage of the Airbus A380.

Kevlar (Aramid) fibers, of diameter $\sim 12 \mu\text{m}$, afford better stiffness, superior toughness and impact resistance than the glass fibers. These have been utilized for composites on prominent and trailing edge panels, beside with fairings for certain traveler aerospace. Kevlar fiber-reinforced composites (KFRCs) indicate the better impact strength and tensile properties, however, owing

Table 5 Commonly used reinforcing agents in aerospace applications

Fiber		Density (g/cc)	Modulus (GPa)	Strength (GPa)	Application areas
Glass	E-glass	2.55	65 to 75	2.2 to 2.6	Radomes; Small traveler a/c components, Interiors of aircraft, Secondary structure; Rocket motor casings
	S-glass	2.47	85 to 95	4.4 to 4.8	Highly loaded components in small traveler a/c
Aramid	Lower modulus	1.44	80 to 85	2.7 to 2.8	Non-load bearing components, Fairings
	Intermediate Modulus	1.44	120 to 128	2.7 to 2–8	Radomes, Certain structural components, Rocket motor casings
	Higher modulus	1.48	160 to 170	2.3 to 2.4	Highly loaded components
Carbon	Standard modulus (high strength)	1.77 to 1.80	220 to 240	3.0 to 3–5	Broadly used for all types of components in a/c, satellites, missiles, antenna dishes, etc.
	Intermediate Modulus	1.77 to 1.81	270 to 300	5.4 to 5.7	Primary components at higher performance fighters.
	High modulus	1.77 to 1–80	390 to 450	2.8 to 3.0 4.0–4.5	Control surfaces in a/c Space components
	Ultra-high strength	1.80–1.82	290 to 310	7.0 to 7.5	Primary components in high performance fighters aircraft and spacecraft

Table 6 Typical composite material systems used in aerospace applications

Material system	Application area
1. Curing at 175°C high strength carbon reinforced epoxy • Zero-bleed (neat resin content) UD prepregs. • 5HS or 8HS bi-directional fabric prepregs. • Good toughness, good self-life and out-life.	Structural parts of helicopters, and fighter aircrafts. e.g., Doors, wing skins, fin, spars, elevons, rudder, and etc. Stiffeners, frames, and rotor blades Structural parts of transport aircraft and helicopters. e.g., Doors, spars, rudder, fin, elevons, and etc.
1. Curing at 175°C moderated modulus carbon reinforced epoxy/BMI/cyanateester • Zero-bleed (neat resin content) UD prepregs • 5HS or 8HS bi-directional fabric prepreg • Good toughness, good shelf-life and out-life • Lower environmental degradation	Stiffeners and frames Radome For Lightning strike protection, wing-skin, and others Fighters fairings, drop-tanks, and fin-radome Small transport aircraft structural components Wing, fuselage, and other
1. Curing at 120°C high strength carbon fiber reinforced epoxy • Zero-bleed (neat resin content) UD prepregs • 5HS or 8HS hi-directional fabric prepreg • toughness, good out-life and shelf-life	
1. Kevlar (aramid) fiber with low loss polyester/cynate esters 2. Cu-mesh epoxy prepregs 3. Epoxy resins with E-glass fabric	
• Higher temperature curing • Room temperature to moderate temperature curing	

to their anisotropic nature they exhibits lower compression strength when related to their carbon and glass fiber counter parts (Rajak *et al.*, 2019; Unterweger *et al.*, 2013).

Conversely in certain applications, better stiffness is essential, hence, CFs are engaged in its place of GFs. Carbon fiber-reinforced polymer composites (CFRP) have originate beneficial in numeral of applications in automobile, aerospace, sports, and other industries (Yi, 2015; Abramovich, 2017; Chung, 2017). Young's modulus increased by 78% and 113%, respectively, when the weight loading of CFs increased from 10% to 30%. The improvements in the cellular structure resulted in the enhanced Young's modulus (Nobe *et al.*, 2019). Carbon fibers with lower diameter (7–10 μm) reveal greater stiffness and strength, which encouraged their widespread use on larger traveler aircraft including Airbus A350 and Boeing 787. Boron fibers with the diameter of 100–140 μm, provide very high stiffness and strength, but its high cost has largely restricted its uses in aerospace structure. Table 5 associates the precise stiffness and strength of a choice of fiber reinforcements and traditional metals such as aluminum and steel.

The combination of high specific modulus and specific strength CFRPs has resulted in their prime use on the modern traveler aircraft. CFs are generally prepared from the carbonization of spun and exceedingly aligned precursor polymer filaments, using either polyacrylonitrile (PAN), pitch or rayon. Synthetic PAN is generally prepared using acrylonitrile (CH_2CHCN) by free radical polymerization. It's the extensively used precursor material, at around 90% of the precursor market, and it results in the highest quality fibers.

Graphene fibers are a new type of high-performance carbonaceous fibers that possesses good tensile strength and higher electrical conductivity when compared to those of carbon fibers. Numerous superior properties of graphene fibers display their potentiality in a diversity of applications, including conductive cables and wires with lower weight, knittable super-capacitors, actuators, micro-motors, solar cell textiles, etc. (Xu and Gao, 2015; Sreenivasulu *et al.*, 2018). The molecular dynamics simulation of graphene reinforced polymer nanocomposites revealed enhances in shear modulus, Young's modulus, and hardness by 27.6%, 150%, and 35%, respectively. Further, a reduction in the coefficient of friction and abrasion rate by 35% and 48% respectively was achieved (Li *et al.*, 2017).

In certain applications, apart from less weight, higher performances are one of major prominence in aerospace structures, e.g., aircraft interiors, equipment enclosures, cockpit, coatings, heat shrinkage tubing, crew gear, space durable mirrors, shrouds, housings, nozzles and substrates for solar array. Composite materials afford good chemical resistance and fire retardancy apart from the benefit of low working cost owing to its lightweight (Peng, 2011).

There are three main shortcomings limits its feasibility of composite materials in most of the aerospace structural components.

- (1) High electrical resistance can lead to restrict EMI shielding, antennas, circuits and lightning strike protection applications (Rathod *et al.*, 2017).
- (2) Poor thermal conductivity of the composite materials rises the load on deicing systems founded on electrical heaters.
- (3) Generally composite materials are poor resistant to impact and be distressed from absorption of moisture, degradation against environment and aging by time (Mahieux, 2006; Martin, 2008).

Depending upon the polymer matrices and reinforcement used, several solutions have been accessible by nano-composites to overwhelm these shortcomings. Some of the polymer nano-composites and their air-craft applications are discussed in the later section.

Merits and Demerits of Polymer Composites in Aerospace Applications

1. Merits of composites:

- Weight reduced 20%–40% with definite strength properties.
- Owing to the light weight fuel consumption is lower.
- Probable for prompt production development cycles.
- Lower coefficient thermal expansion behavior.
- Capability to meet rigorous dimensional stability.
- Better fracture and fatigue resistance over the ceramics and metals.
- Better impact resistance and good damage tolerance increases accident survivability.
- Mechanical properties be able to alter by "lay-up" techniques, with narrowing thicknesses of reinforcing cloth and cloth orientation.
- Advanced polymer composite materials are good corrosion resistance properties than metals.

2. Demerits of composites:

- Higher recurring and non-recurring costs.
- Higher material costs.
- High fabrication costs.
- Non-visible impact damage.
- Repairs are diverse than those to metal structures.

Thermoplastic Composites in Aerospace Applications

Thermoplastics are an alternative to thermoset polymers used in the development of composites and hold promise for increasing production rates. Unlike composites prepared with thermoset polymers, thermoplastic composites do not require a curing step after consolidation, in which the composite is formed by applying heat and pressure to multiple prepregs layers to form a solid laminate. Thermoplastic composites simply essential to be heated up past the melting point of the thermoplastic matrix, consolidated and cooled, unlike thermoset composites which require a curing time for polymer cross-links to form network molecular structure (Barile *et al.*, 2020; Marsh, 2007, 2013).

Table 7 Most commonly used thermoplastic polymers in aerospace applications

Chemical name	T_g ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	Crystallinity	Main characteristics	Cost ($\text{€}/\text{Kg}$)	Sector
Poly ether imide (PEI)	215	–	Amorphous	Outstanding FST properties; Restricted chemical resistance	15–20	Aerospace Interiors
Poly ether sulfide (PES)	220	–	Amorphous	Toughness; low density	1–3	LFT; flexible Pipes
Poly ether ether Ketone (PEEK)	140–145	334–343	Semi-crystalline	Superior chemical resistance; High thermal performance	60–80	Aerospace; Medical
Poly phenyl sulfide (PPS)	85–90	275–290	Semi-crystalline	Excellent chemical resistance	15–25	Aerospace; Industrial

Thermoplastic composites for aerospace applications use high-performance thermoplastic resins, including polyetheretherketone (PEEK), polyetherketoneketone (PEKK), polyaryletherketone (PAEK), polyetherimide (PEI) and polyphenylene sulfide (PPS) (Red, 2014; Gardiner, 2010; Macdonald, 2018; Olson; Favaloro, 2017). Aerospace thermoplastic composites typically have percentages of carbon fiber around 50%–60% by volume. The ratio of carbon fiber to thermoplastic resin is tailored to attain the preferred mechanical properties and compatibility with the manufacturing process. A higher ratio of fiber to resin is desirable for maximizing mechanical performance, but may be more suitable for manufacturing processes with longer cycle times and higher pressures. Lower ratios of fiber to resin may accommodate faster process cycles and lower pressures.

Polyaryletherketones (PAEKs) are prepared by linking the ether groups with ketone groups and the mode these functional are organized in the ultimate molecule categorizes the several parts of the family. The proportion of ketone group decides the melting temperature. They are semi-crystalline thermoplastic polymers with a wide-ranging of melting temperature, high stiffness, strength, and higher resistance to hydrolysis, which mark them appropriate for several applications challenging extreme circumstances.

Polyetheretherketone (PEEK), are one of the most substantial thermoplastic polymers used for fabrication of aerospace structural components. These PEEK structures are designed specifically from the replication of 2 ether groups and 1 ketone group. The existence of aromatic rings and ketone group deliberate a definite degree of rigidity to the PEEK structure, diminished though by the inclusion of ether linkages. For this intention, PEEK devours the low melting temperature than that of other similar compounds including PEK or PEKK. Table 7 show the major properties and cost of the thermoplastic polymers most widely used in aerospace structural applications. In addition, it's worthy to discuss that the PEKK as semi-crystalline thermoplastic polymers which is recently evolving for a broader range of applications, including the probable construction of primary aerospace structures through out-of-autoclave fabrication processes. Diverse properties of PEKK and PEEK, are owing to their different molecular structures, which denote that PEKK reveals good compression strength of up to 80% and broader processing parameters than that of PEEK. Further, the melting temperature of PEKK possesses in the range between 280 $^{\circ}\text{C}$ and 390 $^{\circ}\text{C}$ and T_g of 150–165 $^{\circ}\text{C}$. The specific molecular structure of PEKK donates to greater fusion properties when compared with those of other polymers and metal, which prompted fascinating applications. PEKK can be placed at zenith of the PAEK class, which provide the distinctive chemical, physical and mechanical properties (Barile *et al.*, 2020).

Thermosetting Composites

Thermosetting polymer composites are extensively used subdivision of the PMC that undergo an irreversible polymerization process that facilitates molecular cross-linking during fabrication. The physical and mechanical properties of thermosetting polymer matrices are given in Table 8. Before dealing that the thermosetting polymers that mark up the matrix composite are generally combined of individual macromolecules that stream reasonably free from a liquid or soft tacky solid under the heating. Then these are cured at higher temperature and pressure with or without catalysts to fabricate the cross-linked polymer composites. In order to design a suitable composites structure for aerospace applications, it's significant to realize the properties of both the resin polymers and fiber reinforcements that subsidize to the complete composite performance (Falzon and Pierce, 2020; Hamerton and Kratz, 2018; Black, 2004; McConnell, 2009).

In aerospace sectors, numerous advanced thermosetting resins are most apparently utilized, amongst which epoxy resins are one of most predominant and well-studied. Epoxy resins afford a wider range of gorgeous properties, such as high definite stiffness and strength, and excellent fatigue and corrosion resistance (Toldy *et al.*, 2011; Alagar *et al.*, 1999; Bondzic *et al.*, 2006; Brocks *et al.*, 2013; Vengatesan *et al.*, 2011; Devaraju *et al.*, 2013a; Selvi *et al.*, 2019; Ashok Kumar *et al.*, 2002). By the adding the additives such as thermoplastic polymers to further enhance the properties including impact strength, toughness and moisture resistance. The appropriate epoxy formulations can be used to increase the service temperatures as high as 120 $^{\circ}\text{C}$, which is essential to meets the desires of sub-sonic aerospace structures. Though, thermal degradation of the epoxy resin turn into tricky for high temperature areas such as the nacelle and engine structures, or the aerodynamic sides of supersonic aircraft, where specific resins must be used. Usually, epoxy resins are high cost than the vinyl ester and polyester resins, predominantly when enriched with extraordinary performance additives. For interior of the cabin, where mechanical performance is less significant though the resistance to fire and lower emission of smoke are crucial, phenolic resins are usually employed. These are moderately low cost when compared with

Table 8 Physical and mechanical properties of thermosetting polymer matrices

Properties	Epoxy	Phenolic	BMI	Cyanate ester	Phenolic triazine resin	PBZ's
Density (g/cm ³)	1.20–1.25	1.24–1.32	1.20–1.30	1.10–1.35	1.25	1.19
Maximum use temperature (°C)	180	200	~200	150–200	300	130–280
Tensile strength (MPa)	90–120	24–25	50–90	70–130	4.2	100–125
Tensile modulus (GPa)	3.1–3.8	3–5	3.5–4.5	3.1–3.4	4.1	3.8–4.5
Elongation (%)	3.0–4.3	0.30	3.0	2–4	2.0	2.30–2.90
Dielectric constant (1 MHz)	3.8–4.5	4.1	3.4–3.7	2.7–3.0	3.1	3.0–3.5
Curing temperature (°C)	RT–180	150–190	220–300	180–250	177–316	160–220
Cure shrinkage (%)	>3	~0	~0	~3	~3	~0
TGA onset (°C)	260–340	300–360	360–400	400–420	410–450	380–400
T _g (°C)	150–220	170	230–380	250–270	300–400	170–340
G _{IC} (J/m ²)	54–230	760	160–250	786	120	70–300
K _{IC} (MPa√m)	0.6	1.01	0.85	0.3–1.45	0.2–03	0.6–1.1

similar kind of fire-resistant techniques, and deliver better thermal stability, high strength, good dimensional stability and good resistance to creep at the low cost and reduced mechanical properties when compared to that of epoxy resins.

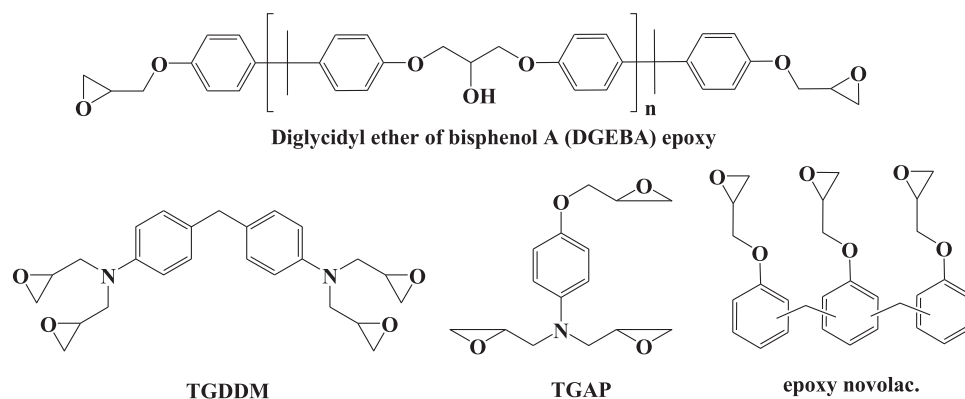
Cyanate ester are another specialized thermosetting material that are usually used in composites for aerospace antennae/radomes owing to its greater electrical properties. They afford greater toughness, strength, minimal moisture absorption, good thermal stability and high fire retardancy properties however these resins are comparatively costly (Falzon and Pierce, 2020; Hamerton and Kratz, 2018; Black, 2004; Fang and Shimp, 1995; Hamerton and Hay, 1998; Saxena and Maiti, 2020; Lockney, 2008; Hay *et al.*, 1989; Simpson *et al.*, 1991; Chen *et al.*, 1997; Harvey *et al.*, 2017; Iredale *et al.*, 2017). Therefore, their usage is fairly restricted. The effort to the superior resin properties, including good damage tolerance and high thermal stability, has directed to significant interest in other interesting polyimide (PI), bismaleimide (BMI) and benzoxazine (BZ) resins that can be mainly more costly. PI polymeric resins needed high temperature and pressure for processing, along with a long curing cycle, and display superior processing difficulties including release of volatile gas and moisture during polymerization. Conversely, these polymeric resins resulted in a greater thermal properties compared to epoxy resins; which joined with better chemical resistant and good adhesion properties marks them ultimate for low weight fabrication, missile and jet engine components. The meticulously BMI resins reveal comparably high thermal stability and are utilized on high enactment aircraft including the F35 Lightning II Joint Strike Fighter.

Benzoxazines are widely utilized for aerospace applications wherever hot/wet performance or resistance to fire is crucial constraint, although these resins persist comparatively new one when compared to that of other resins and were formerly proposed for interiors of aerospace structures. Also BZs afford abundant potential for hybridization with epoxies, phenolics or BMI owing to their molecular structure with reactivity. These matrices can accomplish better fire resistance and mechanical properties due to the higher percentages of aromatic segments and higher molecular than those of phenolics/epoxies and less expensive than BMI (Kiskan, 2018; Ghosh *et al.*, 2007; Ishida and Froimowicz, 2017; Ishida and Agag, 2017; Santhosh Kumar and Reghunadhan Nair, 2010; Devaraju *et al.*, 2019). Consideration for the expenditures in associated with handling, storage, processing, layup, finishing and repairing, it has been advised that BZs might be even inexpensive with epoxy resins. This may owing to its room temperature stability, which contradicts the necessity for ice-covered storage and thawing.

Epoxy Composites for Aerospace Applications

Epoxy resins are attracted as one of the significant thermoset resins widely used as matrices in almost all of the advanced composites system due to their easy changing of the physical state from a lower viscosity to a high melting solid, a extensive range of materials with distinctive properties including good adhesion/impregnation to fiber, ensuing in admirable chemical, and mechanical properties, electrical resistance and minimal shrinkage during curing. Due to diverse physico-chemical, and mechanical stuffs make them appropriate for a widespread range of engineering and other sectors including paints and coating, construction and flooring, food packaging, automotive and public transports, water pipe works, energy, electronics and ICT, sports and aerospace.

The most usual and most broadly deliberated epoxy is the diglycidyl ether of bisphenol-A and its accessible in a different variety of molecular weights ($n = 0.2, 400 \text{ g/mol}$ to $n > 12, 4200 \text{ g/mol}$). Tri-functional epoxy for example TGAP (Scheme 1) result in high cross-linking density and are a mutual constituent in recent epoxy formulations, being co-cured with diglycidyl ether of bisphenol-A. The usage of epoxidized novolacs are able to achieve the high cross linking densities result in higher T_gs (Scheme 1). The presence of higher amount of aromaticity prominent to excellent thermal properties and good abrasive resistance. The typical 1st generation aerospace epoxy materials was prepared using tetra functional epoxy as tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and 4,4'-diaminodiphenyl sulfone (DDS) as hardener (curative) resulted in highly thermally stable cross-linked network structures. Though relatively these epoxy network possesses brittle in nature. This may be overcome with the



Scheme 1 Typical epoxy resins used in aerospace applications.

use of suitable elastomers (e.g., butadiene acrylonitrile elastomer with terminated carboxyl group) and certain engineering thermoplastics including polyethersulfones oligomer with terminal amine groups.

The first usage of epoxy composites in the aircraft components in the year 1970s. They used boron filled epoxy composites for the fabrication of empennages skins of US fighter airplanes namely F14/F15. At the beginning, epoxy composite materials were utilized only in secondary components of aircraft parts, then quickly engineers recognized epoxy composites are more appropriate to making the primary structures of aircraft including fuselages and wings, to enhance the overall properties of the aircraft. Actually, F15 aircraft they used ~2 wt% of composite materials, in F18 it increased to 19 wt% and in F22 further increased to 24 wt%. Its not taking longer time for viable aircrafts to trail the routes of trailblazing defense applications. European Airbus Corporation seen their prospective early in the 1980s, in progress to work composite materials in certain of its viable aircrafts including Airbus A300 and A310.

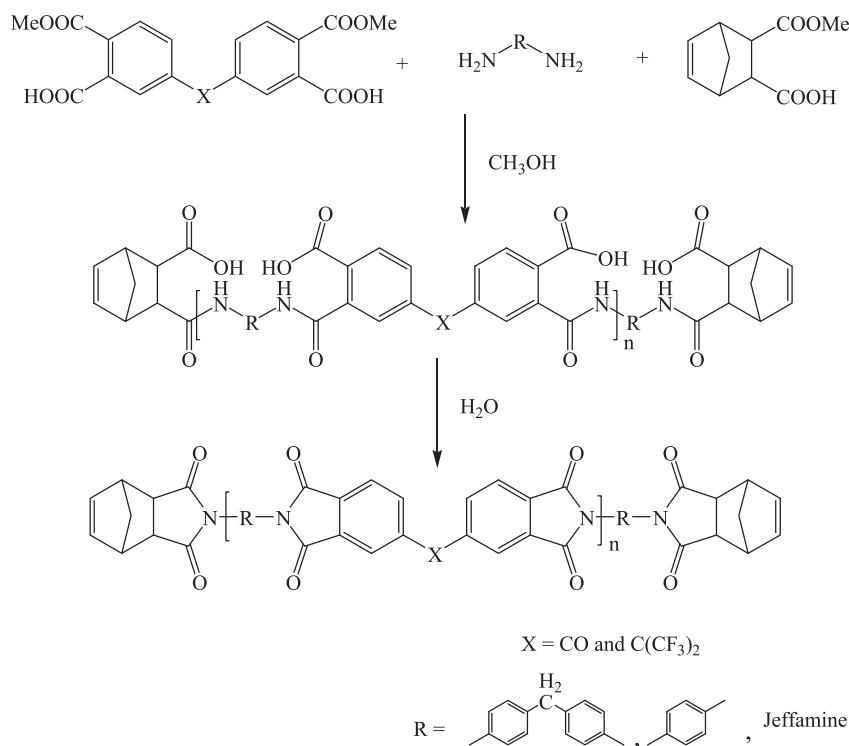
Use of epoxy in the aircraft.

- (1) Reduced weight.
- (2) Good fuel economy.
- (3) Heavy duty intermediates.
- (4) Minimal CO₂ emission.
- (5) Improved cabin climate.
- (6) Better airplane's carbon footprint.

Alagar research group (Alagar *et al.*, 1999) have developed two different kinds of siliconized epoxy hybrid matrix using DGEBA epoxy and hydroxyl terminated polydimethylsiloxane (PDMS). The weight percentage PDMS in epoxy matrix was optimized based on physico-chemical, thermal, mechanical, and electrical properties. The siliconized epoxy matrices cured with different hardeners including polyamidoamine, aromatic amine, aliphatic amine, and 3-aminopropyltriethoxysilane (APTMS). Later, the optimized siliconized epoxy matrix are reinforced with various fillers and additives such as SiO₂, BaSO₄, and TiO₂, dioctylphthalate (plasticizer), tris (2-chloropropyl) phosphate (flame retardant additive) and Kevlar-49 and E-glass fiber (reinforcement) and studied their thermal, mechanical and electrical properties. Inclusion of siloxane fragments in to epoxy systems show improved electrical properties with minimal reduction of mechanical stability. Additives and reinforcements enhanced the electrical and mechanical properties to substantial extent. From the results, disclose that the fiber (Kevlar 49 and E-glass) filled siliconized epoxy composites can be utilized in aerospace and other engineering applications.

Toldy *et al.* (2011) research group reported the carbon fiber-reinforced composites from phosphorus-containing reactive amine used as curative, cross-linking agent and flame retardant for both aliphatic and aromatic epoxy systems to achieve the strong necessities on mechanical properties of the aerospace applications. The flame resistance properties was analyzed with suitable tests and cone calorimeter. In addition to the flame resistance, the tensile strength and impact strength and inter-laminar shear strength were checked and reported. The fiber introduced multilayer composites reveal the better mechanical and flame retardancy properties.

Meenakshi and Ananda kumar research group (Shree Meenakshi *et al.*, 2011) reported the development of 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) based phosphorus tetraglycidyl epoxy nanocomposites for aerospace and other high performance applications. 4,4'-Methylenedianiline (DDM) and bis(3-aminophenyl)phenylphosphineoxide (BAPPO) used as hardener(curing agents) for epoxy polymerization. Nanoclay and monofunctional amine terminated polyhedral oligomeric silsesquioxane (POSS) used as nano-filler for epoxy resin. Then they studied the thermal, mechanical, electrical, flame retardant, and moisture absorption properties of the epoxy nano-composites and discussed. From the data obtained, is concluded that the DOPO based epoxy nanocomposites with enhanced mechanical, thermal properties, flame resistant, dielectric properties can be useful in many fields including electronics, automotive, and advanced aerospace applications with improved performance and enhanced longevity.



Scheme 2 Polymerizable monomeric reactants (PMR) concept shown for selected examples (PMR-15, PMR-II-30, and LARC 160).

Development of conductive adhesives through appropriate structural competence is essential to accomplish both electrical and structural adhesive relationship of aerospace structures. In recent past, nano reinforcements including carbon nanotubes (CNTs) are focused in the development of conductive adhesives. The introduction of CNTs in to polymer matrices significantly enhances the mechanical stability and electrical conductivity of the resulting (i.e., epoxy resin) polymers. In this connection, Benoit Simard (Jakubinek *et al.*, 2015) research group reported the structural and conductive adhesive based on single-walled carbon nano-tubes (SWCNTs) introduced in to aerospace-grade epoxy system at low level filling of up to 1 wt% to enrich the electrical conductivity without affecting the structural bonding ability. At lower loading of SWCNTs in to epoxy maintained or improved the tensile strength, though in case of high loading of SWCNT decreased the strength. The lap-shear and peel tests were performed to assess the structural bonding ability in the joints of composites-to-composites, judiciously retained for adhesives comprising 0.5 and 1 wt% SWCNTs. In case of the 0.5 wt% SWCNT loaded epoxy indicated that there is no change in adhesive, peel and lap-shear strength and it retains the properties. While 1 wt% SWCNT introduced epoxy showed peel strength increased to 30% but the lap-shear strength was decreased to 10%–15%. For 1 wt% SWCNT–adhesives, conductivity values was achieved to 10^{-1} – 10^{-3} S m⁻¹. The developed epoxy adhesive with good conductivity will be suitable for aerospace structures.

Polyimides in Aerospace Applications

Polyimides are one of the most important high performance thermosetting polymers owing to their outstanding thermal and thermo-oxidative stability (Saxena and Maiti, 2020; Lockney, 2008; Hay *et al.*, 1989; Simpson *et al.*, 1991; Chen *et al.*, 1997; Harvey *et al.*, 2017; Iredale *et al.*, 2017; Kiskan, 2018; Critchley *et al.*, 1983; Mittal, 1984; Devaraju *et al.*, 2018). Generally, the aromatic PIs containing a heterocyclic imide unit in the polymer backbone can be used in manufacturing current automotive/aerospace sectors and microelectronic device applications. It is the curiosity of both industrial and academic research to expose the most favorable approaches for making PI materials custom-made to these budding manufacturing comforts. The reasonably the rigid assembly of PIs provide higher T_g of over the 280°C, good mechanical stability. The linearity and rigidity of the cyclic backbone permits for molecular arrangement. This occurrence consequences in reduced CTE than other thermoplastic polymers with flexible and coiled chains. Furthermore, the morphology of lengthy and linear ordered chains affords good solvent resistance properties to the PIs. The evolution of current technology has postured a frequently increasing requirement for materials that can fit under severe conditions, including higher temperatures. These PIs are notorious for their elevated temperature performance in the range of 400°C and 500°C along with good resistance to almost of the chemicals. They are utilized to substitute the traditional materials of metals, and even iron in several engineering applications. Due to its outstanding thermal and mechanical properties make them useful in many applications including flat panel display, high temperature fuel cells, and aerospace applications including military uses.

Polyimides (PI) are used in the form of films, plastics, laminates, coating materials, and high thermal adhesives. PI's be present in two forms including both thermoplastic and thermosetting form. Depends upon the components of their main chain, PI can be categorized as aliphatic, semi-aromatics, aromatics, thermosets and thermoplastics. Traditional linear PI's possesses a higher melt viscosity that restricts their processing capability and final-use of the applications. To overcome this issue, by introducing reactive end-capping agents and reducing the molecular weight to produce thermosetting polyimide with improved processability.

Thermosetting PI's especially, polymerizable monomeric reactants (PMR) were initially developed in the year 1970s at US Air Force at NASA Langley research center for military applications in order to meet the working temperature of 242–374°C to utilize in aircraft engine nozzle, nacelles, gear cases (helicopter), and missile. Generally, PMR was synthesized using aromatic diamine, a dialkyl ester of tetra-carboxylic acid and a mono-functional nadic ester as end-capping agent and the structure is presented in **Scheme 2**. PMR is named according to the use of aromatic di-anhydride ester and aromatic diamine and are demonstrated by PMR-15 (T_g – 370°C), PMR-II-50 (T_g – 340°C), and LARC RP-46 (T_g – 393°C). PMR chains consist of imide systems terminated with nadic anhydride groups (Hamerton and Kratz, 2018; Black, 2004; McConnell, 2009). However, PMR-15 and comparable variants exhibits better mechanical and thermal properties, they comprise the unsafe nature of methylenedianiline (MDA) as carcinogen, making a potential health and safety concern. In this regard, NASA research group initiated to develop new varieties, using less hazardous monomers. The development of LARC RP-46 in 1991 to replace the PMR-15 with very similar approach using 3,4'-oxydianiline instead of MDA (Hay *et al.*, 1989; Simpson *et al.*, 1991). In order to attain the desirable thermo-mechanical performance, high post-cure temperatures need be employed (for e.g., in PMR-15; curing 24 h at 371°C results in a T_g values of 370°C, while a curing performed 50 h at 1 bar pressure resulted in T_g value of 388°C). The application of autoclave cure restricts the release of pentadiene from the norbornene segments via a retro-Diels-Alder reaction, consequently permitting it to react with maleimide to make the cross-linked networks (Hay *et al.*, 1989). Though, this challenging processing technique confines the broader adoption directed to more difference in the feature of the resulting composites thus produced (mostly for thick components); furthermore, PMR-15 is found to be vulnerable to micro-cracking and thermal spiking (Simpson *et al.*, 1991).

Harvey *et al.* (2017) research group developed PMR-PCy PI oligomer using less hazards 4,4'-methylenbis-(5-isopropyl-2-methylaniline) bisaniline prepared from the *p*-cymene as renewable materials. The developed PMR-PCy possesses high T_g of 323°C, better thermo-oxidative stability, and lower water absorption (3%). As per the quantitative structure activity relationship (QSAR) anticipated less hazards nature of CDA is confirmed with in-vitro analysis for muta-genicity, aquatic toxicity and acute toxicity. CDA is observed to be non-mutagenic (Ames) test, had expected 725 mg/kg in rats for LD_{50} , 299.3 mg/L for EC_{50} . These consequences propose that CDA is no to less hazards to humans. The mixture of extraordinary material properties combined with the less hazards of CDA propose that PMR-PCy might be a feasible non-hazards substitutes for PMR-15 in a diversity of aerospace components.

Advanced composite materials research (YLA U.S.A.) prepares 90% of Unitech's prepregging, for their clients for aerospace applications. Several patented materials are existence manufactured using RP-46, together with a high thermal bearing for a viable aerospace engine and radomes application. Due to its tremendous electrical properties which is the main motivation to chosen by the radomes producer. Phenylethynyl-terminated imides (PETIs) has been another invention of the Langley NASA research group developed high speed public transport, the materials provide low melt viscosity by the inclusion of an unsymmetrical dianhydride and high value of T_g of 330°C (PETI-330) and 365°C (PETI-365) depends on the monomer selected. To make great efforts to achieve for good thermal stability, the non appearance of free diamines marks these materials more gorgeous to several users when compared to that of PMRs, however this is compensated by the challenging fabrication desires such as infusion temperature 280°C and cure temperature 371°C and more costly (Hamerton and Kratz, 2018; Black, 2004).

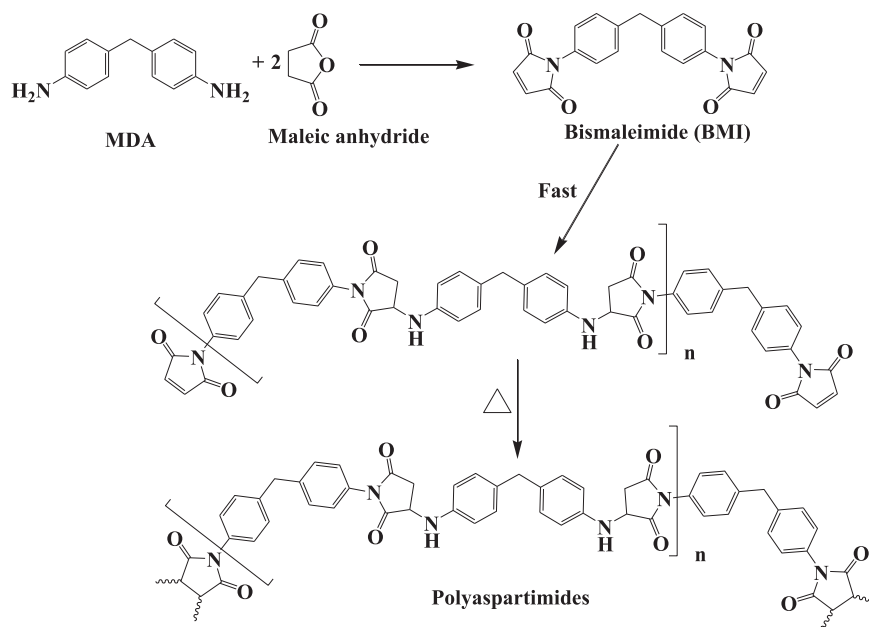
Super imide polyimide is a PMR- type polyimide successfully developed in the early 1990s by Goodrich Corp.'s the chemistry based on high levels of aromaticity with adaptable performance features. It was commercialized in 2000, since the time, over one million fabricated components were used in aerospace applications including aircraft brake and jet engine (Hamerton and Kratz, 2018; Black, 2004). Numerous varieties of Super imide are currently available. Super imide resin based constituents afford high ranks of thermo-oxidative stability, working temperatures over the 343°C. For usages where the thermal spikes are met, Goodrich retains that super imide materials may readily survive tedious thermal spike temperatures of over the 537°C.

Maverick Corp commercialized the 2nd generation non-MDA based PI's. Maverick also trades the conventional, military-qualified MDA-containing PMR II-50, MVK-19, and AFR700 PIs. The Maverick resin has been developed in connection with Glenn research center NASA, with cheap price. The components parts (complex shape) are fabricated using resin transfer molding (RTM), similar to aerospace engine cooling pipes with operative temperatures of 260°C, be able to prepare with interwoven reinforcement. Cured portions reveal higher T_g about 335°C and good thermo-oxidative stability in aerospace engine atmospheres (Black, 2004).

Kapton is an aromatic PI prepared using pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenylether (DDE) to prepare the polyamic acid (PAA) solution, which is later thermal or chemical imidized to get the PI films. For the last 15 years, Kapton PI films has been implemented as the key wire and insulation cable for over the seventy commercial and military airplane, missile and space vehicle uses. This extensive acceptance is owing to their light weight, minimal smoke harmfulness, high electrical properties, good mechanical toughness, resistance to chemicals, and the capacity to survive severe of temperature.

Bismaleimides in Aerospace Applications

Bismaleimides (BMIs) has been the type of PI synthesized from the diamine and maleic anhydride deal lower enactment than PETIs/PMRs. Though the BMIs bridged between epoxies and the PMR polyimides in comparison of cost and properties and are



Scheme 3 Preparation of polyaspartimides (addition polyimides) from Michael addition reaction of BMIs with diamines.

doubtfully the most imperative family of addition PIs assumed more extensive usage in Lockheed Martin's F-22 Raptor and the F-35 Lightning II Joint Strike Fighter but also in civil aerospace sectors. Brittleness is one of key issue of conventional BMIs used in airframes. This issue may be over-whelm by blending with appropriate thermoplastic or elastomeric components. Another method, lowering the cross-link density of BMIs via the development of oligomers to improve the toughness (Kwiatkowski *et al.*, 1975) or the introduction of diamine through Michael addition to produce aspartimides (Scheme 3) (Barton *et al.*, 1994). Though, the introduction of diallylbisphenol-A based co-reactive components (Matrimid 5292 ($T_g = 295\text{--}310^\circ\text{C}$ and $GIC = 195\text{--}217\text{ J/m}^2$)) (Reghunadhan Nair, 2004) or alkenylphenylethers (Compimide TM123, $T_g = 250\text{--}260^\circ\text{C}$ and $GIC = 400\text{--}500\text{ J/m}^2$) (Stenzenberger, 1993) were used to produce second-generation BMIs. Modified BMIs indicate significantly improved toughness that meets equal or higher than that of PIs.

Phthalonitriles in Aerospace Applications

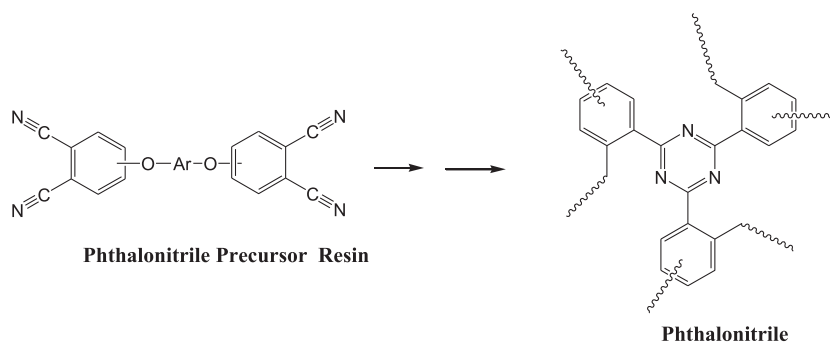
Phthalonitriles are aromatic compounds that produce highly cross-linked network structure which result in excellent thermal stability (Hu *et al.*, 2015). A model scheme for the preparation of phthalonitriles and a highly cross-linked triazine final product are presented in Scheme 4. The length of the oligomeric segments (calculated by O-Ar-O) influences the processing skill, agreeing melting temperatures of $40\text{--}50^\circ\text{C}$ to be attained with an extensive fabrication window of up to 200°C . However once cured at 250°C and post cured at 480°C , the polymer networks indicate no softening $\sim 500^\circ\text{C}$. Moreover, the post cured polymeric material possesses the tremendous short-term contact up to 8 min at the temperature range between 371°C and 538°C . Over the 550°C , phthalonitriles resin carbonized to produce high residue of $>80\%$ at 1000°C . Commercial phthalonitriles (MVK-3), developed by Keller *et al.* in the Naval Research Laboratories (NRL). These are suitable RTM or vacuum-assisted RTM (VRTM) and prepregs (Hamerton and Kratz, 2018).

Carbon fiber and fiber glass reinforced phthalonitrile matrix composites reveal high values of $T_g \sim 450^\circ\text{C}$ and good thermo-oxidative stability over the 371°C as mentioned in the Keller report. The strength especially in fracture toughness and tensile properties of neat phthalonitrile resin showed better or equivalent to the PIs. Phthalonitrile composites showed very high residue and minimal smoke and hazards-gas generation during burning and are only polymer composites to meet the fire resistance properties as per flammability standards of U.S. Navy's (MIL-STD-2031) (Black, 2004).

Eikos Inc. (U.S.A.) has been traded the phthalonitrile resins, which are prepared by in collaboration with JFC Technologies Inc. (U.S.A.). GKN Westland Aerospace Inc. has used woven carbon fabric reinforced phthalonitrile by resin transfer mold for an aircraft engine part to replace the titanium metal. From data obtained from simulated working circumstances for rotor-craft, humidity and temperature, which exhibited that phthalonitrile composites engaged the mechanical properties over the range of -54°C to 343°C and it possesses better performance than that of other resins tested.

Cyanate Esters in Aerospace Applications

Among all cyanate ester (CE) resins are most significant thermosetting polymers developed in the recent past. Cyanate esters have stimulated a wide range of attention because their good performance behavior suitable for number of uses in connection of their



Scheme 4 Schematic representation for polymerization of phthalonitriles.

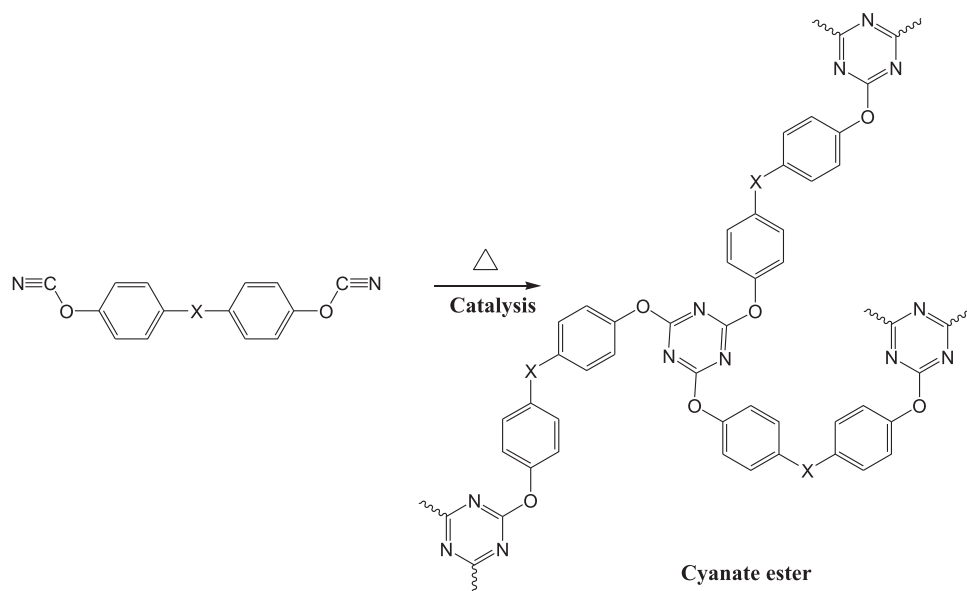
gorgeous physical, high thermal stability, excellent mechanical and electronic properties. These resins are high temperature thermosets and are widely used in structural aerospace, electronics and microwave-transparent composites. A large variability of CE resins with diverse backbone structures with wide range of properties are available. Usually the CE resins is prepared using phenol and cyanogen halide in presence of a mild base (Hamerton, 2004; Bajpai *et al.*, 2020; Fang and Shimp, 1995).

Cyanate esters are remarkable and valuable material towards industrial uses and are polymerized via a cyclotrimerization reaction (Scheme 5) to form a high degree of proficiency, using amine or metallic catalyst be able to reportedly attain the conversions over the 98%. The wide range of properties of CE sorts them versatile and suitable material for utilized in a diversity of applications from aerospace to microelectronics. Aerospace sectors including high thermally stable adhesives and structural components. Their transparency to radar energy and microwave keeps them suitable for conical radome nose cones. Micro-crack and impact resistance characteristics of CE find beneficial for communication satellites, aircrafts components and engine pistons. CE resins and composites are mainly utilized in high-significance applications where enactment at whatever prices is critical. CE resins are widely utilized in high speed printed circuit boards (PCBs), high performance EMI wave entered structural constituents and aerospace components owing to it excellent properties, including low dielectric constant and low dielectric losses, better adhesion strength and mechanical strength, resistance to wet/hot circumstances and processing (Devaraju *et al.*, 2013b; Jothibasu *et al.*, 2012; Zhou *et al.*, 2020; Li *et al.*, 2019). Though, they main shortcoming of high brittle behavior triggered by three dimensional cross-linked networks in the polymerized CE resins. Hence, toughness behavior of cyanate esters needs improvement of impact behavior using suitable polymer modifiers for improved longevity and high performance applications. CEs are superior in thermo-mechanical and hot/wet performance over the epoxy resins, also it directly matches with BMIs in some extents in terms of performance and cast. The processing of CEs quite easy and can be toughened by co-reacting with epoxy resins. Primaset PT resins (phenolic triazines/cyanated novolacs) such as PT30 (Lonza AG) possess similar fire, smoke and toxicity (FST) properties to traditional phenolics but yield high T_g of 400°C (Hamerton and Kratz, 2018). The electrical properties indicated that dielectric constant value of $K \sim 3$ and dielectric loss (dissipation factor) of 0.002–0.003 mark them of specific attention for example, Cycom 5245C and Cycom 5575–2 are engaged in radome structures and in the wing of Rafale fighter jet.

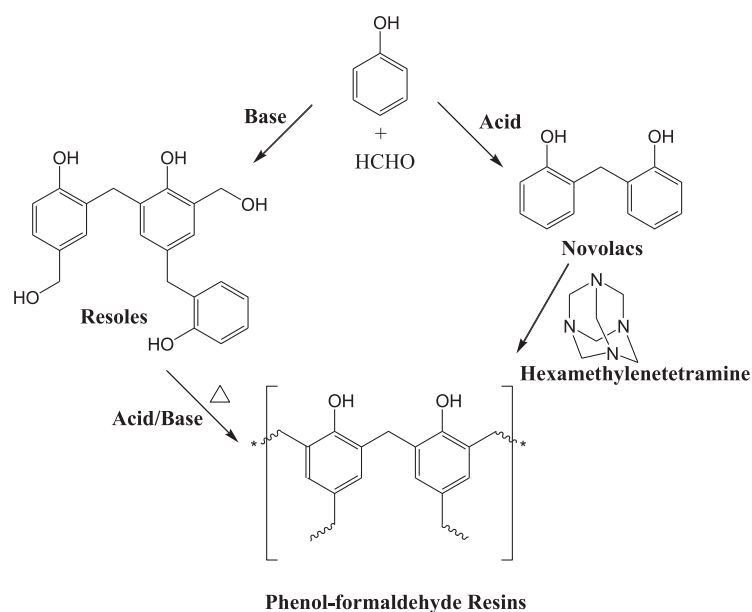
Phenolic Resins in Aerospace Applications

Phenolic resins are one of oldest and traditional synthetic resins and stand up from the innovative effort of Baekeland (Bakeland, 1907). They prepared phenolic resins through poly condensation reactions using phenol and formaldehyde in acidic environment (excess in phenol) to obtain novolacs or under basic environment (excess in aldehyde) to yield resoles (Scheme 6). Both novolacs and resoles are almost the similar type of high aromatic structure with short methylene connections, when combusted, the subsequent thermosets exhibit outstanding thermal stability, flame and heat resistance, minimal-smoke, and minimal toxicity of emission [fire/smoke/toxicity, (FST)] properties than those of other commercial thermosets. These thermal properties are related to resistance to chemical, good mechanical stability, and good retention of properties at high temperatures that mark them gorgeous, while T_g values of polymerized phenolics are comparatively lower (160°C) and by succeeding post cure may exceed 300°C. Over the 300°C some of the degradation of cured phenolic resins is perceived owing to the degradation of low molecular weight components. The phenolic network, consist of polycyclic, graphitic-like aromatic structures, is highly compressed and resulted in carbon-rich residue, therefore, phenolics resins exhibited the higher limiting oxygen index (LOI) value of 32. This specific properties has also directed to the progress of tradition carbon-carbon composites in which the phenolic is purposefully pyrolyzed to form a high residue carbon-carbon composites, which, possesses the enormously higher thermal stabilities (service temperatures over the 2200°C). Even though remaining tradition polymers in terms of prices, the promising thermal and FST performances exhibited by phenolics have much-admired them for utilized in aerospace interiors including flooring, panels, and partitions.

One of the major drawbacks, the brittleness behavior of phenolics restricted their usage in various applications when the structures are exposed to higher amounts of stress and fatigue. This might be overwhelmed by hybridization using elastomers including amine-terminated butadiene liquid oligomer Hypo RLP (Nanoresins, Geesthacht, Germany), carboxyl-terminated



Scheme 5 Schematic representation for polycyclotrimerization of cyanate esters.

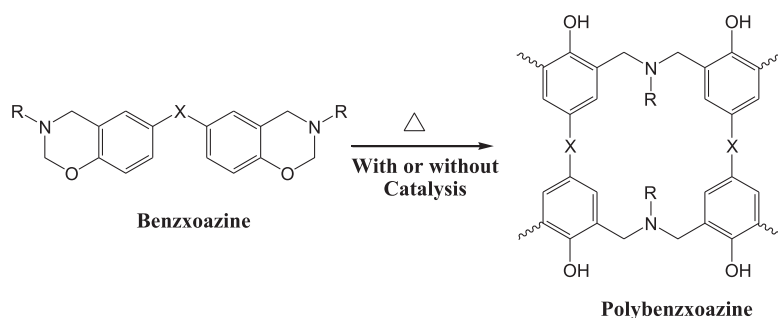


Scheme 6 Preparation and cure of phenol-formaldehyde resins (resoles and novolacs).

butadiene liquid oligomer or silicones (Hypro CTBN 1300 $\times$ 8 (Nanoresins)), and silicone copolymer comprising 40 wt% silicone (Albiflex H 1083 S1 (Nanoresins)) in the form of toughening/flexibilizing agents.

Polybenzoxazines in Aerospace Applications

Polybenzoxazines (PBz's) emerged as one of the superior substitute to conventional phenolics including novolac/resole for the past 3–4 eras. Although PBz's (**Scheme 7**) show structural resemblance to traditional phenolics by some means, the tertiary amine functional deviate the structure and bring the strong inter and intra molecular hydrogen bonding that manage several advantages. These resins display good thermal stability, higher mechanical stability, chemical resistance, low moisture adsorption, minimal or no shrinkage during curing, high residue char, high T_g , and high operating temperatures (Kiskan, 2018; Ghosh *et al.*, 2007; Ishida and Froimowicz, 2017; Ishida and Agag, 2017; Santhosh Kumar and Reghunadhan Nair, 2010; Devaraju *et al.*, 2019). Hence, PBZs have been utilized in several applications in various industry including blends, composites, alloys, printed electronic circuit boards, and etc.



Scheme 7 Scheme for the preparation of polybenzoxazine.

Bi-functional based PBZs have been already commercially prepared by Huntsman, Gurit, Henkel, and Shikoku Chemicals (Hamerton and Kratz, 2018). Huntsman is one of the foremost industry that constantly involved in the development of benzoxazine resins since 1994 specifically for aerospace sectors. Accordingly, this company traded five various types of benzoxazine resins mentioned in Table 9 including with its conventional names and key characteristic properties namely reactivity, viscosity, thermal, and flammability properties (Black, 2004). As perceived from Table 9, these commercial benzoxazines reveals higher T_g , which are significant for aerospace sectors. In addition, mono-functional benzoxazines including aniline and phenol based benzoxazine are also manufactured by Huntsman and exported in the trade name of RD 2007-027 (Mw of 211) and RD 2009-008 (Mw of 419). Though, these benzoxazines are not appropriate for aerospace sectors; thus, they are profitable as benzoxazine accelerators be utilized as a catalyst for homo-polymer benzoxazine and co-polymer in combination with benzoxazine and epoxy. The benzoxazine accelerators are commercially traded with the name of Accelerator DT 300 (mp - 154–156°C) and DT 310 (mp - 127–134°C).

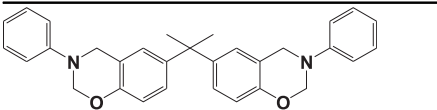
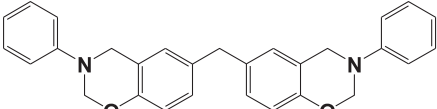
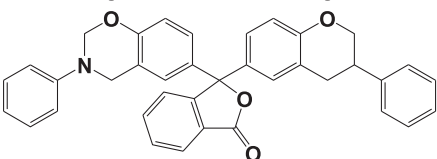
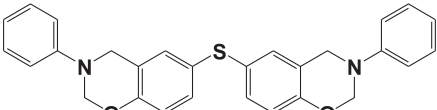
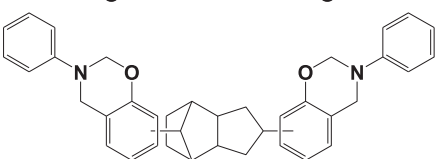
According to Huntsman, benzoxazines are ultimate for various applications including aerospace primary and secondary components such as bulk-heads, interior panels, lavatories, galleys, and table trays. In transport, these benzoxazines might be utilized as automotive components including frames, hood components, panel body, and structural assistances for buses, trucks, and light rail cars. Also, benzoxazine have probable applicability in gas/oil sectors as composites risers, pipes, down hole plugs, and vessels with high-pressure, besides its used as free from halogen laminates in microelectronic application for PCBs. Gurit is a foremost prepregs dealer for aerospace interiors and an innovative aviation sector later 1985. This dealer offered prepregs based on benzoxazine resins for aerospace interiors, traveler, and consignment floors. These prepregs (trade name as PB1000) are free from formaldehyde, and most appropriate wherever environmental standards similar to AIRBUS AP2091 are essential. The polymerization temperature of benzoxazine is as lower as 140°C for 45 min. The polymerized products are free from voids and fulfill the international fire protection (JAR/FAR) guidelines. As per the Gurit, PB1000 be able to utilize as a substitute for phenolics. For example, flexural strength is observed as 320 MPa for PB1000 filled fabrics of 550 this was good comparable to phenolics used for aerospace structures. Furthermore, PB1000 impregnating E-glass fabrics is also commercialized by them. The materials are lightweight with good mechanical and high flame resistance, low smoke, and minimal toxicity (FST) values. This benzoxazine composites might be applicable in both railway and aerospace sectors.

Self-Sensing Composites for Aerospace Applications

Self-sensing polymer composites are ability to sensing their damage, temperature, strain, and etc. (Rana *et al.*, 2014; Wang and Chung, 2013). Presently, self-sensing polymer based composites are received much distinctive consideration for numerous structural applications to ensure better safety aspects. At present, most of the case external sensors are used to distinguishing the status of structural parts. Fiber-optic and piezoelectric sensors are commercially available sensors to detect the damage and strain. Though, these sensing methods have certain intrinsic shortcomings such as high cost, fragile nature, need of expert personnel, inconvenience to isolated places and etc. To overcome these glitches, self-sensing polymer composites are growing in distinction. These composites are ability of sensing damage or strain in the structural components.

Self-sensing polymer composites typically work on the piezo-resistive principle i.e., alter their electrical resistivity with damage or strain. These composites comprise with the conducting filler such as carbon fibers, carbon particles and carbon nanotubes. The alteration of electrical resistivity is owing to the alteration in electrical connection points among the conducting components. Electrical resistivity increased over the tensile loading, this may be owing to the decrease in electrical connection points among the conductive fillers (Rana and Fangueiro, 2016). While composites are exposed to compressive loading the electrical resistivity is decreased. Conversely, in case of long conducting fiber reinforced composites indicated the reduction in resistivity while tensile loading owing to conducting fiber orientation and also more in electrical connection points. Since fiber polymer composites are generally utilized in aerospace and other sectors, evolving long fiber polymer composites with good sensing ability is challenging. Recently, hybrid polymer composites of carbon and other non-conducting fibers have been established to perform detecting the damage of composites. These composites are able to indicate the sharp alteration in the resistance as well as the fracture of the

Table 9 Commercialized benzoxazines by Huntsman corporation

Benzoxazine structure	Trade name	Viscosity at 120° C (cP)	Reactivity at 190° C (min.)	T _g (°C) from DMA	UL-94 (s)
	Araldite® MT 35600	<1000	~15	~180	>250
	Araldite® MT 35600	<1000	~20	160–170	75–100
	Araldite® MT 35600	3000–3500	5–10	230–240	<50
	Araldite® MT 35600	2000–2500	1–2.5	170–180	100–125
	Araldite® MT 35600	3500–4000	10–15	~140	>250

composites. Though, this can accomplish strain sensing by appropriate sensitivity in the pre-stressed situations. To overwhelm this issue, carbon particles or CNTs have been utilized to accomplish the good sensing enactment. The CNT reinforced polymer composites can able to detect even damage at micro-scale in composite parts and, consequently, are highly favorable for self-sensing of aerospace applications.

Self-Healing Polymer Composites for Aerospace Applications

Self-healing polymers are able to repair the destruction commenced within their structure spontaneously (Rana and Figueiro, 2016; Blaiszik *et al.*, 2010). The self-healing of destruction may be extrinsic, i.e., the composites comprise an exterior healing agent for destruction repair. The healing agent can be enclosed within the microcapsules, hollow fibers/or vascular networks. Owing to beginning of cracks, these structures that comprise healing agents breakdown, liberating the healing materials and revamping the damages. Fig. 3 displays the self-healing mechanism based on microcapsule.

Typically in epoxy matrix composites diverse types of microcapsules are prepared and used as self-healing agent. Generally, urea-formaldehyde are used for the production of microcapsules (Blaiszik *et al.*, 2008; Brown *et al.*, 2003; Yang *et al.*, 2012, 2011; Coope *et al.*, 2011; Guadagno *et al.*, 2010). Microcapsules prepared using triethylenetetramine (TETA) for wear-resistant (Khun *et al.*, 2014) and poly (methyl methacrylate) (PMMA) microcapsules for high thermal and storage stability (Li *et al.*, 2013), are prepared and utilized. Numerous encapsulation methods are used to develop self-healing materials. Though, the research has mostly motivated on meltable dispersion, interfacial and in-situ encapsulation methods. Meltable dispersion, healing agents are dispersed in the melted polymer to prepare the micro-capsules after solidification (Rule *et al.*, 2005). Interfacial and *In-situ* polymerization methods are used for preparation of urea-formaldehyde or TETA microcapsules. In this method, the shell is prepared by polymerization at the interface of healing agent droplets and the oil-in-water emulsion. The synthesis of nano-capsules using an ultra-sonication approach can also be attained. The common techniques of healing is depicted in Fig. 3.

Self-healing also can happen by numerous intrinsic mechanisms. In intrinsic self-healing, the developed with certain polymer composites which be able to reveal reversible connections by certain external triggers such as light, heat, radiation and etc., Consequently, upon beginning of damage, the external triggers can prompt diverse sorts of reversible connections (eg, a reversible chemical bonding like Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions (Scheme 8)), reversible physical connections in ionic polymers, supramolecular attractions, shape memory connections etc. and repair the flaws. The healing effectiveness of polymer composites is calculated by the following equation: Numerous revocable chemical reactions are discovered for self-healing applications. The most widely studied chemical reactions are the rDA. Scheme 8 shows the self-healing mechanism of

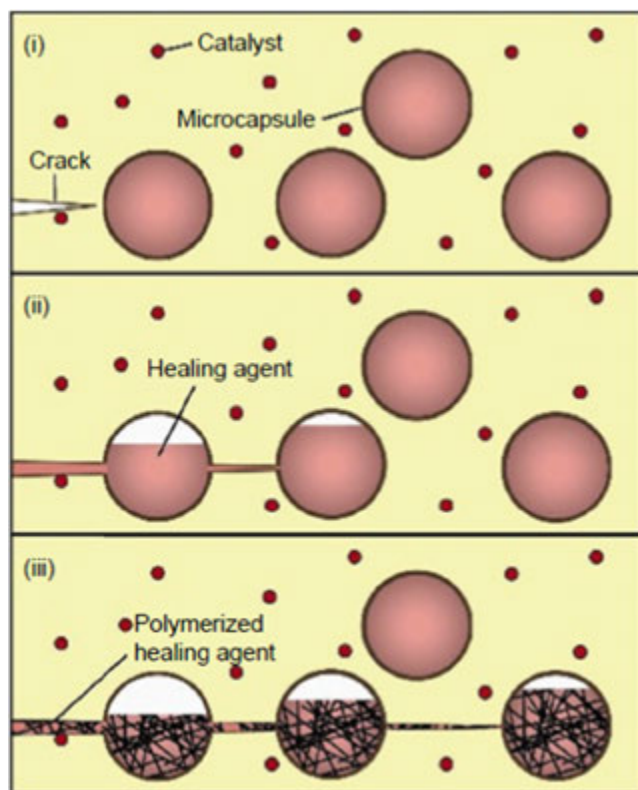
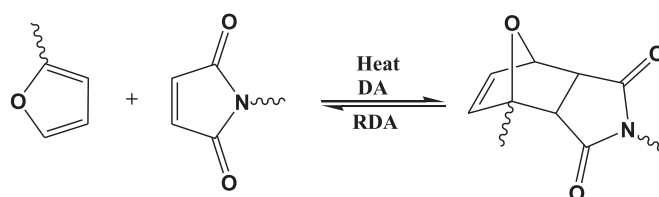


Fig. 3 Schematic model for microcapsule-based self-healing mechanism. Copyright 2016. Reproduced with permission from In: Rana, S., Figueiro, R. (Eds.), 2016. *Advanced Composite Materials for Aerospace Engineering Processing, Properties and Applications*. Woodhead Publishing Series in Composites Science and Engineering. Elsevier, from Elsevier.



Scheme 8 Diels - Alder (DA) reaction mechanism for cross-linked polymers.

DA-rDA reaction of polymerization and damage for cross-linked DA polymers. [Chen *et al.* \(2003\)](#) reported the self-healing ability of maleimide and furan polymers. BMI tetrauran can be utilized to make a thermally triggered self-healing carbon fiber composites, through the DA reaction and electrical resistive heating of carbon fibers ([Park *et al.*, 2010](#)). This composites exhibited almost 100% strength retrieval under definite circumstances.

$$\text{Healing efficiency} = \frac{f_{\text{healed}} - f_{\text{damaged}}}{f_{\text{virgin}} - f_{\text{damaged}}}$$

Where f is the property of interest. The self-healing composites be able to repair the subsequent properties:

- (1) Fatigue property,
- (2) Fracture property,
- (3) Impact energy,
- (4) Corrosion and barrier property.

Polymer Nanocomposites for Aerospace Applications

Polymer nanocomposites (PNCs) have attracted considerable devotion in aerospace sectors over the few decades. PNCs comprising of both polymer matrix and nano-reinforcement dispersed into polymer matrix. Nano-fillers might be of different natures (nano-platelets, nano-tubes/nano-fibers/nano-wires, nano-particles, and fullerenes), and with at least one measurement need be in

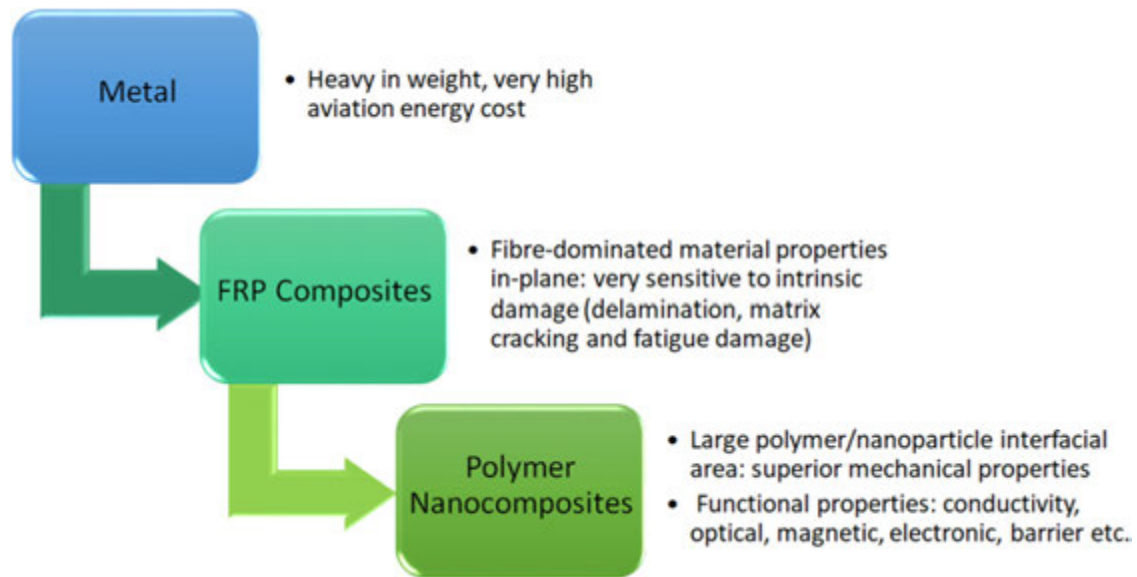


Fig. 4 Evolution of materials for aerospace structures.

Table 10 Commonly used nano-materials and their efficient properties related to aerospace applications

S. No	Functional properties	Nano-materials
1.	Mechanical and scratch resistance	Al ₂ O ₃ , SiO ₂ , ZrO ₂
2.	Antimicrobial	CuO, TiO ₂ , ZnO
3.	Gas barrier	Nano-clays, graphene
4.	Corrosion	Nano-clays
5.	Conductivity	Graphene, CNTs, SnO ₂
6.	Fire resistant	Nano-clays
7.	Heat (thermal) stability	CNTs, ZrO ₂
8.	Ultraviolet stability	TiO ₂ , ZnO, BaSO ₄ , CeO ₂ , graphene
9.	Impact properties	SiO ₂ , TiO ₂ , CaSiO ₃ , Al ₂ O ₃ , CNTs, clay

1–100 nm range. Nano reinforcement offers very good interfacial area for superior adherence to matrix which eventually leads to greater enrichment on the property of PNCs. Unlike traditional filler reinforced polymer systems, PNCs need comparatively and significantly lower loadings of nano-fillers. Owing to its high surface area and high aspect ratio, the small amount of nano-materials are reinforced in to polymer matrix, which greatly enhance the composites properties, which reduce the further weight of the product which creates them a vital aspirant for aerospace uses. Besides, nano-material-based polymer nano-composites can offer numerous multifunctional behaviors including better thermal stability, good fire resistance, good electrical properties, optical properties, field emission, improved durability, good impact properties, and etc., which are mostly substantial for aerospace applications (Rana and Fangueiro, 2016; Thostenson *et al.*, 2005b). Fig. 4 designates the progress of materials used for aerospace structures. Recently, studies have revealed the prospective enhancement in the performance and properties of nano-reinforced polymer materials in which nano-scale materials including clay, silica particles, single-walled and multi-walled carbon nano-tubes (SWCNTs and MWCNTs), graphene, metal nano-particles and etc., are incorporated.

However, these polymer nano-composites can't able to meet the strength desires for primary aerospace components. Although certain nano-materials such as CNTs and CNFs have extraordinarily good mechanical stability than the traditional reinforcing materials similar to carbon fibers, the restriction on attaining a high volume fraction of nano-materials in composites does not permit them to attain high mechanical strength comparable to those of traditional fiber-reinforced composites (Rana and Fangueiro, 2016; Rana *et al.*, 2015). At high volume portion, nano-materials are exceedingly problematic to disperse within the polymer matrix and attempt to agglomeration, creating voids and flaws in the resulting composites. So, the easy technique to attain good mechanical strength with multifunctional behavior is to progress hybrid composites that combine both traditional and nano-reinforcements. Numerous studies on polymer nano-composites (PNCs) have been revealed that nano-fillers can deliver several functional properties (Rana and Fangueiro, 2016). Table 10 lists certain of the nano-materials with possible functional properties for aerospace uses.

The Air Force Office of Scientific Research (AFOSR, USA) newly underwrote a project to examine how the nano-fillers can increase the erosion resistant properties and heat transfer performances of solid rocket nozzle ablatives. They tried with three types of nano-particles including cloisite montmorillonite (MMT) nano-clay, carbon nano-fibers and polyhedral oligomeric silsesquioxane (POSS) were used as nano reinforcement in to resole-type phenolic matrix. All the nano-composite trials, composed with an standard ablative material, were employed in a lab scale solid rocket motor device skillful of making an exhaust plume with abrasive aluminum oxide particles, with flame temperatures $\sim 2200^{\circ}\text{C}$ and plume velocity of roughly 2000 m/sec. Data resulted from the nano-fillers reinforced nano-composites exhibited enhanced erosion resistance properties. Carbon nano-fiber reinforced nano-composites indicated the lowest erosion rate of 28% than that of other nano-composites systems. Heat-soaked temperature measurements also are lesser in the case nano-composite systems when compared to the standard ablative material. Polymer nano-composites grasp great potential for forthcoming high-temperature applications though the utmost task is to choose the nano-particles with good compatibility with polymeric resin (Black, 2004).

Summary and Conclusion

The use of polymer matrix based composites in the aerospace sectors are increasing progressively owing to numerous added benefits of composites over the metals, including reduction in weight, good strength, good resistance to corrosion and greater fracture and fatigue properties with less fuel consumption. The present article provides an overview of several types of polymer matrices including both thermosetting and thermoplastic polymers, various reinforcements including glass/carbon/Kevlar/aramid fibers and their properties including advantages and disadvantages for making aerospace primary and secondary structures. The article also discusses the necessity and importance on developing consistent self-healing and self-sensing composites to prevent the repairs and to increase the safety aspects and service life of aerospace components. Nonetheless, it can be projected that polymer matrix materials with vast flexibility in terms of structural materials and properties will substitute the metal components in the future aerospace applications. Moreover, the modern generation of traveler air-crafts has incorporated a larger amount of composite components in primary aerospace structures, assembly up to $> 50\%$. The development of bigger parts with better complexity, to report the higher production volumes in these modern generation composite aircraft, needed substantial revolution in the arena of polymer composites.

References

- Abramovich, H., 2017. Chapter 9 – Stability of composite stringer-stiffened panels. In: Abramovich, H. (Ed.), *Stability and Vibrations of Thin Walled Composite Structures*. Sawston and Cambridge: Woodhead Publishing, pp. 461–507.
- Alagar, M., Thanikaivelan, T.V., Ashok Kumar, A., Mohan, V., 1999. Synthesis and characterization of high performance polymeric hybrid siliconized epoxy composites for aerospace applications. *Materials and Manufacturing Processes* 14 (1), 67–83.
- Alimuzzaman, S., 2014. Nonwoven Flax Fibre Reinforced PLA Biodegradable Composites. University of Manchester.
- Ashok Kumar, A., Alagar, M., Rao, R.M.V.G.K., 2002. Synthesis and characterization of siliconized epoxy-1,3-bis(maleimido)benzene intercrosslinked matrix materials. *Polymer* 43 (3), 693–702.
- Bajpai, A., Saxena, P., Kunze, K., 2020. Tribo-mechanical characterization of carbon fiber-reinforced cyanate ester resins modified with fillers. *Polymer* 12 (1725), 1–13.
- Baekeland, L.H., 1907. Method of making insoluble products of phenol and formaldehyde. U.S. Patent No. 942699.
- Barbero, E.J., 2017. *Introduction to Composite Materials Design*. CRC Press.
- Barile, M., Lecce, L., Iannone, M., Pappadà, S., Roberti, P., 2020. Revolutionizing aircraft materials and processes. In: Pantelakis, S., Tserpes, K. (Eds.), *Revolutionizing Aircraft Materials and Processes*. Springer International Publishing, pp. 14–87.
- Barton, J.M., Hamerton, I., Rose, J.B., Warner, D., 1994. The synthesis, characterization and polymerization kinetic study of a series of related addition polyimides. *High-Performance Polymers* 6, 21–34.
- Black, S., 2004. Are high-temp thermosets ready to go commercial? *High-Performance Composites*. Available at: <https://www.compositesworld.com/articles/are-high-temp-thermosets-ready-to-go-commercial>.
- Blaiszik, B.J., Sottos, N.R., White, S.R., *et al.*, 2008. Nanocapsules for self-healing materials. *Composites Science and Technology* 68 (3–4), 978–986.
- Blaiszik, B.J., Kramer, S.L.B., Olugebefola, S.C., 2010. Self-healing polymers and composites. *Annual Review of Materials Research* 40 (1), 179–211.
- Bondzic, S., Hodgkin, J., Krstina, J., Mardel, J., 2006. Chemistry of thermal ageing in aerospace epoxy composites. *Journal of Applied Polymer Science* 1 (100), 2210–2219.
- Brooks, T., Shiino, M.Y., OdilaHilárioCioffi, M., JacobusCornelisVoorwald, H., CaporalliFilho, A., 2013. Experimental RTM manufacturing analysis of carbon/epoxy composites for aerospace application: Non-crimp and woven fabric differences. *Materials Research* 16 (5), 1175–1182.
- Brown, E.N., Moore, J.S., White, S.R., Sottos, N.R., 2003. Fracture and fatigue behavior of a self-healing polymer composite. In: Simon, U. (Ed.), *Bioinspired Nanoscale Hybrid Systems*. Materials Research Society, pp. 101–106.
- Brown, G., 2014. The Use of Composites in Aircraft Construction. Available at: <http://vandaair.com/2014/04/14/the-use-of-composites-in-aircraft-construction>.
- Cantor, B., Assender, H., Grant, P., 2015. *Aerospace Materials*. Boca Raton: CRC Press.
- Carey, J., Melenka, G., Hunt, A., *et al.*, 2016. Braided composites in aerospace engineering. In: Figueiro, R., Rana, S., *et al.* (Eds.), *Advanced Composite Materials for Aerospace Engineering*. Elsevier, pp. 175–212.
- Chalmers, D.W., 1991. Experience in design and production of FRP marine structures. *Marine Structures* 4, 93–115.
- Chen, X.X., Wudl, F., Mal, A.K., Shen, H.B., Nutt, S.R., 2003. New thermally emendable highly cross-linked polymeric materials. *Macromolecules* 36 (6), 1802–1807.
- Chen, X.B., Fu, Y., Li, P., 1997. A study on thermo-oxidative stability of non-MDA PMR polyimide composites. In: *Proceedings of ICCM–11*, pp. 765–771.
- Chung, D.D.L., 2017. Introduction to carbon composites. In *Carbon Composites: Composites with Carbon Fibers, Nanofibers, and Nanotubes*. Amsterdam: Elsevier Science, pp. 88–160.
- Clyne, T., Withers, P., 1995. *An Introduction to Metal Matrix Composites*. Cambridge University Press.
- Coope, T.S., Mayer, U.F.J., Wass, D.F., Trask, R.S., Bond, I.P., 2011. Self-healing of an epoxy resin using Scandium(III) triflate as a catalytic curing agent. *Advanced Functional Materials* 21 (24), 4624–4631.

- Critchley, J.P., Knight, G.J., Wright, W.W., 1983. Heat Resistant Polymers. New York: Plenum Press.
- Devaraju, S., Alagar, M., 2018. Unsaturated Polyester – Macrocomposites. Elsevier.
- Devaraju, S., Selvi, M., Alagar, M., 2018. Synthesis and characterization of thermally stable and flame retardant hexakis (4-aminophenoxy) cyclotriphosphazene-based polyimide matrices. *International Journal of Polymer Analysis and Characterization* 23 (1), 29–37.
- Devaraju, S., Krishnadevi, K., Sriharshitha, S., Alagar, M., 2019. Design and development of environmentally friendly polybenzoxazine–silica hybrid from renewable bio-resource. *Journal of Polymers and the Environment* 27, 141–147.
- Devaraju, S., Vengatesan, M.R., Selvi, M., Song, J.K., Alagar, M., 2013a. Hyperbranched polysiloxane-based diglycidyl ether of bisphenol a epoxy composite for low k dielectric application. *Polymer Composites* 34, 904–911.
- Devaraju, S., Vengatesan, M.R., Selvi, M., Song, J.K., Alagar, M., 2013b. Mesoporous silica reinforced cyanate ester nanocomposites for low k dielectric applications. *Microporous and Mesoporous Materials* 179, 157–164.
- Falzon, B.G., Pierce, R.S., 2020. Chapter 3 – Thermosetting composite materials in aerostructures. In: Pantelakis, S., Tserpes, K. (Eds.), *Revolutionizing Aircraft Materials and Processes*. Springer International Publishing, pp. 87–114.
- Fang, T., Shimp, D., 1995. Polycyanate esters: Science and applications. *Progress in Polymer Science* 20, 61–118.
- Favaloro, M., 2018. Thermoplastic Composites in Aerospace – The Future Looks Bright. Available at: <https://www.compositesworld.com/articles/thermoplastic-composites-in-aerospace-past-present-and-future>.
- Gardiner, G., 2010. Aerospace-Grade Compression Molding. Available at: <https://www.compositesworld.com/articles/aerospace-grade-compression-molding>.
- Ghosh, N.N., Kiskan, B., Yagci, Y., 2007. Polybenzoxazines – New high performance thermosetting resins: Synthesis and properties. *Progress in Polymer Science* 32, 1344–1391.
- Guadagno, L., Longo, P., Raimondo, M., *et al.*, 2010. Cure behavior and mechanical properties of structural self-healing epoxy resins. *Journal of Polymer Science Part B: Polymer Physics* 48 (23), 2413–2423.
- Hamerton, I. (Ed.), 2004. *Chemistry and Technology of Cyanate Ester Resins*. Dordrecht: Springer.
- Hamerton, I., Hay, J.N., 1998. Recent technological developments in cyanate ester resins. *High-Performance Polymers* 10, 163–174.
- Hamerton, I., Kratz, J., 2018. The use of thermosets in modern aerospace applications. In: Qipeng, G. (Ed.), *Thermosets Structure, Properties, and Applications*, second ed. Elsevier, pp. 303–340.
- Harvey, B.G., Yandek, G.R., Lamb, J.T., *et al.*, 2017. Synthesis and characterization of a high temperature thermosetting polyimide oligomer derived from a non-toxic, sustainable bisaniline. *RSC Advances* 7, 23149–23156.
- Hay, J.N., Boyle, J.D., Parker, S.F., Wilson, D., 1989. Polymerization of N-phenyl nadimide: A model for the crosslinking of PMR-15 polyimide. *Polymer* 30, 1032–1040.
- Hu, J., Liu, Y., Jiao, Y., *et al.*, 2015. Self-promoted phthalimide-containing phthalonitrile resins with sluggish curing process and excellent thermal stability. *RSC Advances* 5, 16199–16206.
- Hull, D., Clyne, T.W., 1996. *An Introduction to Composite Materials*. Cambridge University Press.
- Iredale, R.J., Ward, C., Hamerton, I., 2017. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. *Progress in Polymer Science* 69, 1–21.
- Ishida, H., Froimowicz, P., 2017. *Advanced and Emerging Polybenzoxazine Science and Technology*. John Fedor Publisher, Elsevier.
- Ishida, H., Agag, T., 2017. *Handbook of Benzoxazine Resins*. Elsevier.
- Jakubinek, M.B., Ashrafi, B., Zhang, Y., *et al.*, 2015. Single-walled carbon nanotube–epoxy composites for structural and conductive aerospace adhesives. *Composites Part B: Engineering* 69, 87–93.
- Jothibasur, S., Devaraju, S., Venkatesan, M.R., *et al.*, 2012. Thermal, thermomechanical and morphological behavior of Octa (maleimido phenyl) silsesquioxane (OMPS)-cyanate ester nanocomposites. *High-Performance Polymers* 24 (5), 379–388.
- Kesarwani, S., 2017. Polymer composites in aviation sector a brief review article. *International Journal of Engineering Research & Technology* 6, 518–525.
- Khun, N.W., Sun, D.W., Huang, M.X., Yang, J.L., Yue, C.Y., 2014. Wear resistant epoxy composites with diisocyanate-based self-healing functionality. *Wear* 313 (1–2), 19–28.
- Kiskan, B., 2018. Adapting benzoxazine chemistry for unconventional applications. *Reactive and Functional Polymers* 129, 76–88.
- Kwiatkowski, G.T., Robeson, L.M., Brode, G.L., Bedwin, A.W., 1975. Thermosetting diphenyl sulfone-based maleimides. *Journal of Polymer Science: Polymer Chemistry Edition* 13, 961–972.
- Li, Q., Mishra, A.K., Kim, N.H., *et al.*, 2013. Effects of processing conditions of poly(methylmethacrylate) encapsulated liquid curing agent on the properties of self-healing composites. *Composites Part B: Engineering* 49, 6–15.
- Li, W., Huang, W., Kang, Y., *et al.*, 2019. Fabrication and investigations of G-POSS/cyanate ester resin composites reinforced by silane-treated silica fibers. *Composites Science and Technology* 173, 7–14.
- Li, Y., Wang, S., Wang, Q., 2017. A molecular dynamics simulation study on enhancement of mechanical and tribological properties of polymer composites by introduction of graphene. *Carbon* 111, 538–545.
- Liu, Y., Du, H., Liu, L., Leng, J., 2014. Shape memory polymers and their composites in aerospace applications: A review. *Smart Materials and Structures* 23 (2), 023001.
- Lockney, D., 2008. Polyimide Boosts High-Temperature Performance. NASA. https://spinoff.nasa.gov/Spinoff2008/ip_5.html.
- Lubin, G., 2013. *Handbook of Composites*. Springer.
- Macdonald, J., 2018. Using Thermoplastics in Aerospace Applications. Available at: <https://www.aerodefensetech.com/component/content/article/adt/features/articles/32727>.
- Mahieux, C.A., 2006. *Environmental Degradation in Industrial Composites*. Chicago, IL: Elsevier.
- Mangalgi, P., 1999. Composite materials for aerospace applications. *Bulletin of Materials Science* 22 (3), 657–664.
- Marsh, G., 2007. Airbus takes on Boeing with reinforced plastic. *Reinforced Plastics* 51 (11), 26–27.
- Marsh, G., 2013. Bombardier throws down the gauntlet with CSeries airliner. *Reinforced Plastics* 55 (6), 22–26.
- Martin, R., 2008. *Ageing of Composites*. Cambridge: Woodhead Publishing.
- McConnell, V.P., 2009. Resins for the hot zone, part 1: Polyimides. *High-Performance Composites*. Available at: <http://www.compositesworld.com/articles/resins-for-the-hot-zone-part-1-polyimides>.
- Mittal, K.L. (Ed.), 1984. *Polyimides Synthesis, Characterization, and Applications*. US: Springer.
- Mouritz, A., Bannister, M., Falzon, P., Leong, K., 1999. Review of applications for advanced three-dimensional fibre textile composites. *Composites Part A: Applied Science and Manufacturing* 30 (12), 1445–1461.
- Mouritz, A.P., 2012. *Introduction to Aerospace Materials*. Elsevier.
- Njuguna, J., 2016. *Lightweight Composite Structures in Transport: Design, Manufacturing Analysis and Performance*. Woodhead Publishing.
- Njuguna, J., Pielichowski, K., 2003. Polymer nanocomposites for aerospace applications: Properties. *Advanced Engineering Materials* 5 (11), 769–778.
- Nobe, R., Qiu, J., Kudo, M., Ito, K., Kaneko, M., 2019. Effects of SCF content, injection speed, and CF content on the morphology and tensile properties of microcellular injection-molded CF/PP composites. *Polymer Engineering & Science* 59, 1371–1380.
- Nurhaniza, M., Ariffin, M.K.A., Ali, A., Mustapha, F., Noraini, A.W., 2010. Finite element analysis of composites materials for aerospace applications. *IOP Conference Series: Materials Science and Engineering* 11, 012010.
- Olson, E., 2017. Thermoplastic Composites for Aerospace Applications. Available at: <https://insights.globalspec.com/article/12596/thermoplastic-composites-for-aerospace-applications>.

- Park, J.S., Darlington, T., Starr, A.F., *et al.*, 2010. Multiple healing effect of thermally activated self-healing composites based on Diels-Alder reaction. *Composites Science and Technology* 70 (15), 2154–2159.
- Peng, H.X., 2011. Polyurethane nanocomposite coatings for aeronautical applications. In: Leng, J., Lau, A.K.T. (Eds.), *Multifunctional Polymer Nanocomposites*. Boca Raton: CRC Press, pp. 337–387.
- Prakash, S., 2019. Experimental investigation of surface defects in low-power CO₂ laser engraving of glass fiber-reinforced polymer composite. *Polymer Composites* 40, 4704–4715.
- Quilter, A., 2001. *Composites in Aerospace Applications*. IHS. (IHS White Paper).
- Rajak, D.K., Pagar, D.D., Menezes, P.L., Linul, E., 2019. Fiber-reinforced polymer composites: Manufacturing, properties, and applications. *Polymers* 11 (1667), 1–37.
- Rana, S., Figueiro, R. (Eds.), 2016. *Advanced Composite Materials for Aerospace Engineering Processing, Properties and Applications*. Woodhead Publishing Series in Composites Science and Engineering. Elsevier.
- Rana, S., Parveen, S., Figueiro, R., 2015. Advanced carbon nanotube reinforced multiscale composites. In: Bafekrpour, E. (Ed.), *Advanced Composite Materials: Manufacturing, Properties, and Applications*. De Gruyter Open.
- Rana, S., Zdraveva, E., Pereira, C., Figueiro, R., Correia, A.G., 2014. Development of hybrid braided composite rods for reinforcement and health monitoring of structures. *The Scientific World Journal* 2014, 1–9.
- Rathod, V.T., Kumar, J.S., Jain, A., 2017. Polymer and ceramic nanocomposites for aerospace applications. *Applied Nanoscience* 7, 519–548.
- Ratina, D., Karger-Kocsis, J., 2008. Recent advances in shape memory polymers and composites: A review. *Journal of Materials Science and Technology* 43 (1), 254–269.
- Red, C., 2014. The outlook for thermoplastics in aerospace composites, 2014–2023. In *High-Performance Composites*. Cincinnati: Gardner Business Media, Inc., pp. 54–63.
- Reghunadhan Nair, C.P., 2004. Advances in addition-cure phenolic resins. *Progress in Polymer Science* 29, 401–498.
- Rule, J.D., Brown, E.N., Sottos, N.R., White, S.R., Moore, J.S., 2005. Wax-protected catalyst microspheres for efficient self-healing materials. *Advanced Materials* 17 (2), 205–208.
- Santhosh Kumar, K.S., Reghunadhan Nair, C.P., 2010. *Polybenzoxazines: Chemistry and Properties*. SmithersRapra Technology.
- Saxena, D., Maiti, P., 2020. Polymer composites in aerospace applications. In: Pawar, Shivaji (Ed.), *Progress and Prospects in Nanoscience Today*. New York: Nova Science Publishers, Inc, pp. 59–76.
- Selvi, M., Devaraju, S., Alagar, M., 2019. Cyclotriphosphazene nanofiber-reinforced polybenzoxazine/epoxy nanocomposites for low dielectric and flame-retardant applications. *Polymer Bulletin* 76, 3785–3801.
- Shree Meenakshi, K., Pradeep Jaya Sudhan, E., Ananda Kumar, S., Umapathy, M.J., 2011. Development and characterization of novel DOPO based phosphorus tetraglycidyl epoxy nanocomposites for aerospace applications. *Progress in Organic Coatings* 72, 402–409.
- Simpson, M., Jacobs, P.M., Jones, F.R., 1991. Generation of thermal strains in carbon fiber reinforced bismaleimide (PMR-15) composites: Part 3. A simultaneous thermogravimetric mass spectral study of residual volatiles and thermal microcracking. *Composites* 22, 105–112.
- Sreenivasulu, B., Ramji, B., Nagaral, M., 2018. A review on graphene reinforced polymer matrix composites. *Materials Today: Proceedings* 5, 2419–2428.
- Stenzenberger, H.D., 1993. Recent developments of thermosetting polymers for advanced composites. *Composite Structures* 24, 219–231.
- Subramani, P., Rana, S., Oliveira, D.V., Figueiro, R., Xavier, J., 2014. Development of novel auxetic structures based on braided composites. *Materials and Design* 61, 286–295.
- Taj, S., Munawar, M.A., Khan, S., 2007. Natural fiber-reinforced polymer composites. *Proceedings of the Pakistan Academy of Sciences* 44 (2), 129–144.
- Thomas, S., Joseph, K., Malhotra, S.K., Goda, K., Sreekala, M.S. (Eds.), 2012. *Polymer Composites: Volume 1 Macro and Microcomposites*, first ed. Wiley.
- Thostenson, E.T., Li, C., Chou, T.-W., 2005a. Nanocomposites in context. *Composites Science and Technology* 65, 491–516.
- Thostenson, E., Li, C., Chou, T., 2005b. Review nanocomposites in context. *Journal of Composites Science and Technology* 65, 491–516.
- Toldy, A., Szolnoki, B., Marosi, G., 2011. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. *Polymer Degradation and Stability* 96 (3), 371–376.
- Toozandehjani, M., Kamarudin, N., Dashtizadeh, Z., *et al.*, 2018. Conventional and advanced composites in aerospace industry: Technologies revisited. *American Journal of Aerospace Engineering* 5 (1), 9–15.
- Unterwieser, C., Brüggemann, O., Fürst, C., 2013. Synthetic fibers and thermoplastic short-fiber-reinforced polymers: Properties and characterization. *Polymer Composites* 35, 227–236.
- Velosa, J., Rana, S., Figueiro, R., *et al.*, 2012. Mechanical behavior of novel sandwich composite panels based on 3D-knitted spacer fabrics. *Journal of Reinforced Plastics and Composites* 31, 95–105.
- Vengatesan, M.R., Devaraju, S., Alagar, M., 2011. Studies on thermal, mechanical and morphological properties of organoclay filled azomethine modified epoxy nanocomposites. *High-Performance Polymer* 23, 3–10.
- Waheedullah Ghorri, S., Siakeng, R., Rasheed, M., Saba, N., Jawaid, M., 2018. *The Role of Advanced Polymer Materials in Aerospace*. Woodhead Publishing Series in Composites Science and Engineering. Elsevier. pp. 19–34.
- Wang, D., Chung, D.D.L., 2013. Through-thickness piezoresistivity in a carbon fiber polymer-matrix structural composite for electrical-resistance-based through-thickness strain sensing. *Carbon* 60 (1), 129–138.
- Wang, R.-M., Zheng, S.-R., Zheng, Y.-P. (Eds.), 2011. *Polymer Matrix Composites and Technology*. Woodhead Publishing Series in Composites Science and Engineering. Elsevier.
- Williams, G., Trask, R., Bond, I., 2007. A self-healing carbon fibre reinforced polymer for aerospace applications. *Composites Part A: Applied Science and Manufacturing* 38 (6), 1525–1532.
- Xu, Z., Gao, C., 2015. Graphene fiber: A new trend in carbon fibers. *Materials Today* 18, 480–492.
- Yadav, R., Tirumali, M., Wang, X., Naebe, M., Kandasubramanian, B., 2020. Polymer composite for antistatic application in aerospace. *Defence Technology* 16, 107–118.
- Yan, C., Lifeng, W., Jianyue, R., 2008. Multi-functional SiC/Al composites for aerospace applications. *Chinese Journal of Aeronautics* 21 (6), 578–584.
- Yang, T., Wang, C.H., Zhang, J., He, S., Mouritz, A.P., 2012. Toughening and self-healing of epoxy matrix laminates using mendable polymer stitching. *Composites Science and Technology* 72 (12), 1396–1401.
- Yang, Z., Wei, Z., Le-ping, L., Hong-mei, W., Wu-jun, L., 2011. The self-healing composite anticorrosion coating. *Physics Procedia* 18, 216–221.
- Yi, X.S., 2015. Development of multifunctional composites for aerospace application. In: Friedrich, K., Breuer, U. (Eds.), *Multifunctionality of Polymer Composites*. Oxford: William Andrew Publishing, pp. 367–418.
- Zhou, Z.-X., Li, Y., Zhong, J., *et al.*, 2020. High-performance cyanate ester resins with interpenetration networks for 3D printing. *ACS Applied Materials & Interfaces* 12 (34), 38682–38689.

Tribology of Polymer Matrix Composites Within the Automotive Industry

Leonardo I Farfan-Cabrera and Monica Tapia-Gaspar, Tecnológico de Monterrey, Escuela de Ingeniería y Ciencias, Monterrey, México

José Pérez-González, Instituto Politécnico Nacional, Escuela Superior de Física y Matemáticas, Ciudad de México, México

© 2021 Elsevier Inc. All rights reserved.

Introduction

Automotive industry represents an important sector of the world economy and a large end-use customer market for the polymer industry, which has resulted in increased production and quality of these materials. In 2017, the market for global automotive composite materials was estimated around \$4.3 billion, one and a half its value of \$2.8 billion in 2011 (Kazmierski, 2012), which represents a substantial growth for the world chemical and composites industries. According to a recent report by the Economics & Statistics Department of the American Chemistry Council (American Chemistry Council, 2019), only the North American Free Trade Agreement (NAFTA) light vehicle industry was valued around \$431 billion in 2018. The 16.81 million light vehicles assembled in the United States, Canada and México in that year required about 2.6 billion kg of plastics and polymer matrix composites (PMCs) valued in \$7.7 billion, or \$458 per vehicle. This is in line with the trend for higher fuel efficiency and lower gas emissions in vehicles, which is partially achieved by using more and more lightweight materials such as aluminum, magnesium and PMCs to replace heavy metals, such as iron and steel in different automotive components. As a reference, the total weight of a lightweight vehicle in 2008 comprised 7.8% of aluminum and 8.4% of PMCs meanwhile the total weight of a vehicle in 2018 had 10.7% of aluminum and 8.8% of PMCs. The use of PMCs in light vehicles has increased from less than 9 kg per vehicle in 1960 to about 160 kg per car in 2018 distributed in more than 1000 components (American Chemistry Council, 2019). In the same line, demands from European Union legislation have promoted the production and use of vehicles with increased fuel efficiency and lower emissions (from <130 g CO₂/km in 2015 down to <95 g CO₂/km by 2021), which is being mainly attained by vehicle weight reduction using PMCs. The use of these light materials allows a reduction of weight in the range of 15%–25% in the case of glass-fiber reinforced composites and 25%–40% for carbon-fiber reinforced composites (Suschem, 2017).

The light vehicle market presents significant opportunities for plastics and composites. The trends of world automotive industry to move up to self-driving electric vehicles and ride-sharing electric platforms will demand for increased safety and new vehicle architectures, which will create new exclusive opportunities for plastics and composites, fostering their production this way. Currently, the most typical PMCs found in cars, minivans, pickups and SUVs are made of a polymer matrix, commonly polyester, polyurethane, epoxy, polypropylene, nylon, or other resin, and fibrous reinforcements made of different materials such as glass, carbon, aramid, etc. The fibers provide strength and stiffness while the matrix protects, and transfers loads between fibers. This synergy allows the production of materials with superior attributes to those found in polymers or fibers alone. Thus, it is possible to find PMCs in different automobile parts such as the exterior body and interior components, safety devices and structures, electrical systems, chassis, fuel system, powertrain and engine components in today's vehicles. The latest are the most complex and complicated parts since they are not only subjected to stress, vibrations, fatigue and environmental changes, but also to friction and wear, and are exposed to chemical fluids such as combustible, lubricants and coolants.

PMCs used in components to be exposed to friction and wear during operation are known as tribological PMCs. These can be formed by molding or casting, injection molding or vulcanization to provide lighter, cheaper, quieter and corrosion and wear resistance components for vehicles (Fox, 2016). Basically, in the case of tribological composites, the matrix provides the bulk mechanical properties and the service temperature while the reinforcements, apart from improving stiffness, impact resistance, thermal conductivity and creep resistance at high temperatures, they are intended to improve wear resistance and reduce friction coefficient (Friedrich *et al.*, 1995) by lowering adhesion and rising stiffness and strength (Friedrich, 1997; Reinicke *et al.*, 1998; Aldousiri *et al.*, 2013).

Polymers may be roughly classified into three classes according to their physical properties, operation temperature range and cost, these are commodity, mid-range and high-performance polymers (Fox, 2016). Commodity plastics such as polystyrene, polyvinyl chloride, polypropylene and polyethylene in its various forms are relatively weak materials with tensile strengths in the order of 20 MPa and operating temperature range below 100°C. The mid-range polymers, commonly referred to as engineering polymers, include materials such as polyamides and polyesters as polyethylene and polybutyl terephthalate with strengths up to 75 MPa and continuous operating temperatures up to 120°C. Finally, the third class, or high-performance polymers, are polymers with strengths in the range of 100 MPa and operating temperature of hundreds of degrees (<427°C) along with a series of outstanding physical properties as high melting point and excellent resistance to degradation. The most remarkable examples of these polymers are polyaramids (e.g., Kevlar) and the polyaryletherketone family which includes polyetheretherketone and polybenzimidazole. Currently, engineering and high-performance polymers (both thermoplastics and thermosets, and elastomers) reinforced with fibers are the most used to produce a number of different tribological polymer composites for automotive components such as tires, seals, gears, dry sliding bearings, rolling bearings, brakes and clutch materials, paint coats, etc. For the sake of space, this article is limited to tribological components made of PMCs apart from those of the interior of modern internal combustion engine and battery electric vehicles, some of which can be identified in Fig. 1(a)–(b).

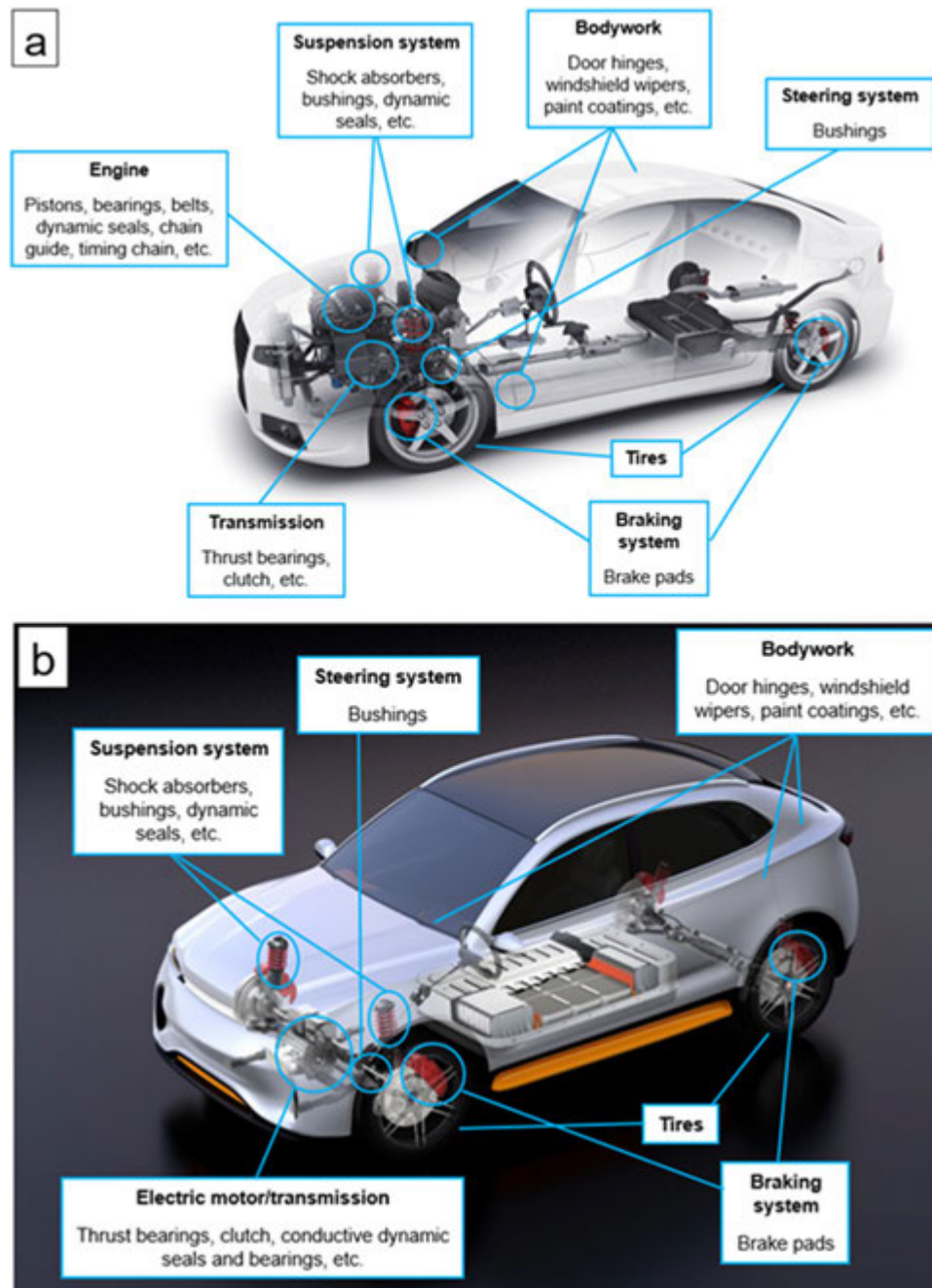


Fig. 1 Typical tribological components made up of PMCs in (a) combustion engine vehicles; (b) battery electric vehicles.

Tribology Fundamentals of Polymer Composites

Friction is defined as the resistance encountered by one body in moving over another either in sliding or rolling motion. To slide or roll one body against the other, a tangential force, F , is needed, which is known as the frictional force. The ratio between the frictional force and the normal load, W , acting on the bodies is known as the friction coefficient, μ , given as:

$$\mu = \frac{F}{W} \quad (1)$$

The friction coefficient is dependent on many factors as surface roughness, temperature, humidity, mechanical properties of contacting materials, lubricant and lubrication type. High values of μ are undesirable in most of engineering applications since they lead to unacceptable high friction forces that result in significant energy losses, heating and wear. Polymers typically exhibit

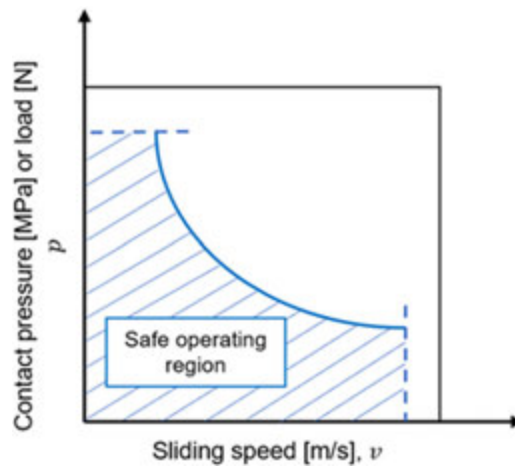


Fig. 2 Schematic representation of a p - v chart emphasizing the safe operating region for a polymer.

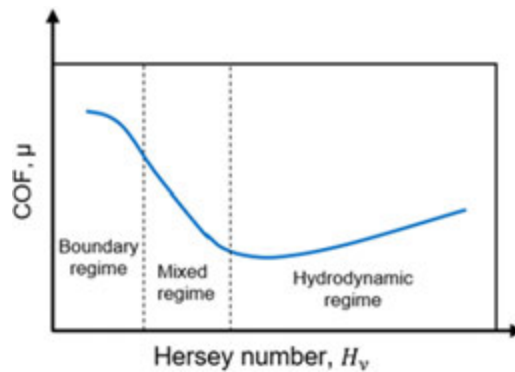


Fig. 3 Schematic representation of a typical Stribeck's curve.

low coefficients of friction (COF), with values ranging between 0.1 and 0.5, whether self-mated or sliding against other materials (Hutchings and Shipway, 2017). This is because polymer/metal or polymer/polymer contact is predominantly elastic and, in some cases, viscoelastic.

Polymer tribology usually does not follow the classic laws of friction, since the COF of polymers varies notably according to normal load (COF decreases with load up to a limit determined by deformation and contact temperature), sliding speed (COF decreases with increasing speed up to a limit determined by heat generation and contact temperature) and temperature (COF varies for temperatures above and below the glass transition temperature, T_g) (Hutchings and Shipway, 2017). In general, fillers in PMCs generate an increase of COF, so special techniques should be applied to reduce friction in PMCs. Among the most popular solutions for this purpose are the inclusion of soft solid fillers and the addition of internal or external lubricants into a harder polymer matrix. The softer filler/polymer acts as a lubricant facilitating the formation of a transfer film at the interface between the filled polymer and a hard surface (Briscoe and Sinha, 2005). In order to identify reliable tribological conditions (sliding speed and load), and to avoid premature failures for a component made of a PMCs, pressure or load, p , versus speed, v , charts are commonly developed. An example of a p - v chart for a polymer, emphasizing the safe operating region is shown in Fig. 2. The maximum value of contact pressure or load on the curve represents the force limit while the maximum sliding speed value states the frictional heating limit for safe operation of the polymer.

Using lubricants is the most widely spread way to reduce COF between surfaces of polymers and their composites. A lubricant can be a liquid, solid or semisolid substance between the sliding or rolling surfaces used to separate them and to avoid surface asperities contact. However, the lubricant may not totally avoid asperity contacts, so different lubrication regimes may be found, these are called hydrodynamic, boundary and mixed regime, respectively. The lubrication regime is represented by the Stribeck's curve illustrated in Fig. 3. It is a graphical representation of the COF as a function of the bearing number or Hersey number, H_v , which is a dimensionless lubrication parameter defined as, $H_v = \eta U/W$, where η is the lubricant viscosity, U is the sliding speed and W is the applied load (Hutchings and Shipway, 2017). Hersey number may be also seen as the ratio between the lubricant film thickness and surface roughness. In the hydrodynamic lubrication regime, the surfaces are completely separated by the

lubricant film preventing asperities contact, while in boundary lubrication the surfaces are not separated completely, and appreciable asperity contact is generated. Mixed lubrication is the combination of both, hydrodynamic and boundary lubrication regimes at the sliding interface.

Asperity contact in sliding interfaces of materials is precursor of wear, which can be generally classified into dry sliding wear and lubricated sliding wear. Both wear types can be subclassified into abrasive and adhesive wear. Abrasive wear can take place in two different ways: two-body abrasion or three-body abrasion. Two-body abrasion is produced mainly by the action of hard asperities, either from one surface or both, while three-body abrasion occurs when separate hard particles, namely, debris and contaminant particles, are present at the sliding interface altering friction and wear. Three-body abrasion is dependent on the particles acting at the interface, these might be either fixed/adhered or dragged to one or both surfaces producing grooves or rolling at the interface. On the other hand, adhesive wear is produced predominantly by adhesion between the surfaces (Hutchings and Shipway, 2017).

A simple assessment of sliding wear is given by the Archard's wear equation (Hutchings and Shipway, 2017):

$$Q = \frac{V_w}{S} = \frac{KW}{H} \quad (2)$$

where Q (mm^3/m units) is known as wear rate or the volume worn (V_w , mm^3 units) per unit sliding distance (S , m units), W is the normal load in N units, H is the hardness of the softer surface and K (mm/m), is the wear coefficient, which represents the severity of the wear processes. In this model, it is assumed that H is equal to the yield pressure for the plastically deforming asperity, akin to that occurring in an indentation, so H has units of N/m^2 . In practice, however, the specific wear rate, k , which is given by $k = K/H$ is more often used. It represents the wear volume per sliding distance per normal load commonly expressed in $\text{mm}^3/\text{m} * N$ units. Although Archard's model was originally developed for metals, it can provide some insight into the wear of other materials, including polymers.

PMCs used in unlubricated tribological applications such as bearings, bushings, gears, etc., usually slide against harder metallic countersurfaces (Friedrich, 2018). Thus, nearly all the deformation due to contact or sliding takes place within the polymer, and the surface finish of the hard countersurface has a strong influence on the mechanism of wear. For smooth countersurfaces adhesive wear is expected in the surface layers of the polymer, while for rough countersurfaces wear results either from abrasion associated with plastic deformation of the polymer by hard asperities, or from fatigue crack growth in the deformed region (Friedrich, 2018). These two classes of wear mechanisms in polymers, involving surface and subsurface deformation have been termed as interfacial and cohesive wear processes, respectively (Hutchings and Shipway, 2017). Interfacial wear involves material removed by processes occurring close to or in the surface of the polymer, mainly, by adhesion. It occurs only when the countersurface is smooth, and there is transfer of polymer to the harder countersurface and its subsequent removal as wear debris, as illustrated in Fig. 4(a). The process is similar to that seen in metals. In steady state wear the wear rate is often directly proportional to the normal load over a large range, in conformity with the Archard's wear equation. On the other hand, cohesive wear is produced by plastic deformation of the surface and subsurface of the polymer, caused by the passage of hard protuberances on the countersurface. There may be asperities on the hard surface arising from its topography, or particles of the harder material partially embedded into a softer countersurface, or possibly protuberances of polymeric debris transferred to the countersurface (Hutchings and Shipway, 2017), as illustrated in Fig. 4(b).

Overall, friction and wear of PMCs can exhibit different behavior according to the polymer matrix (thermoplastic, thermoset or elastomer) and reinforcements. Thermoplastic and fiber thermoplastic composites are known to exhibit distinct tribological behavior from that in thermosets or elastomers. In thermoplastics, film transfer of the soft polymer surface to the metallic surface during sliding due to heating is very likely (Aldousiri et al., 2013). Friction generates heat at the sliding interface, which deteriorates the polymer surface by material detachment when temperature exceeds T_g . The addition of fillers and/or fibers usually influences the heat transfer at the interface by reducing adhesion between the asperities, film transfer and material detachments. In the case of thermoset polymers and fiber thermoset composites, the possibility of film transfer is lower than in thermoplastics since thermosets are, in general, much harder than thermoplastics (Shackelford and Alexander, 2014), reducing the possibility of plastic deformation and film transfer on the countersurface. Neat thermosets promote rougher film transfer than thermoplastics, but the surface is cooler since the frictional force is less and debris is more able to roll at the interface instead of being adhered. The presence of fibers in thermosets are useful to further assist in cooling the interface by strengthening the exposed layer of the polymer and lowering friction due to easier rolling of debris. These effects, however, may increase wear in some cases due to the transition from adhesive to abrasive wear (Aldousiri et al., 2013). On the other hand, friction in elastomers is different from most of thermosets and thermoplastics. It is because in elastomers, besides the interfacial and cohesive transfer, there is one more mode of energy dissipation called hysteresis. The hysteresis loss is characteristic of all viscoelastic materials and comes from the viscoelastic "flow" or deformation of the materials over the asperities of the hard countersurface. For smooth and dry contacts, the interfacial component can be very large in comparison to the hysteresis component; however, for rough surfaces and for smooth and wet surfaces, hysteresis loss contributes substantially to the overall frictional force (Briscoe and Sinha, 2005). In contrast to thermoplastics and thermosets, elastomers exhibit tearing as the main wear mode, even under three-body abrasion situations (Farfan Cabrera et al., 2017b). Tearing consists of a corrugated appearance feature on the elastomer surface produced by micro delaminations perpendicularly orientated to the sliding direction, which result from micromolecular fracture or repeated rupture of the polymer's molecular chains. It is generated under continuous sliding action of hard asperities of the countersurface or debris (Zhang, 1992).

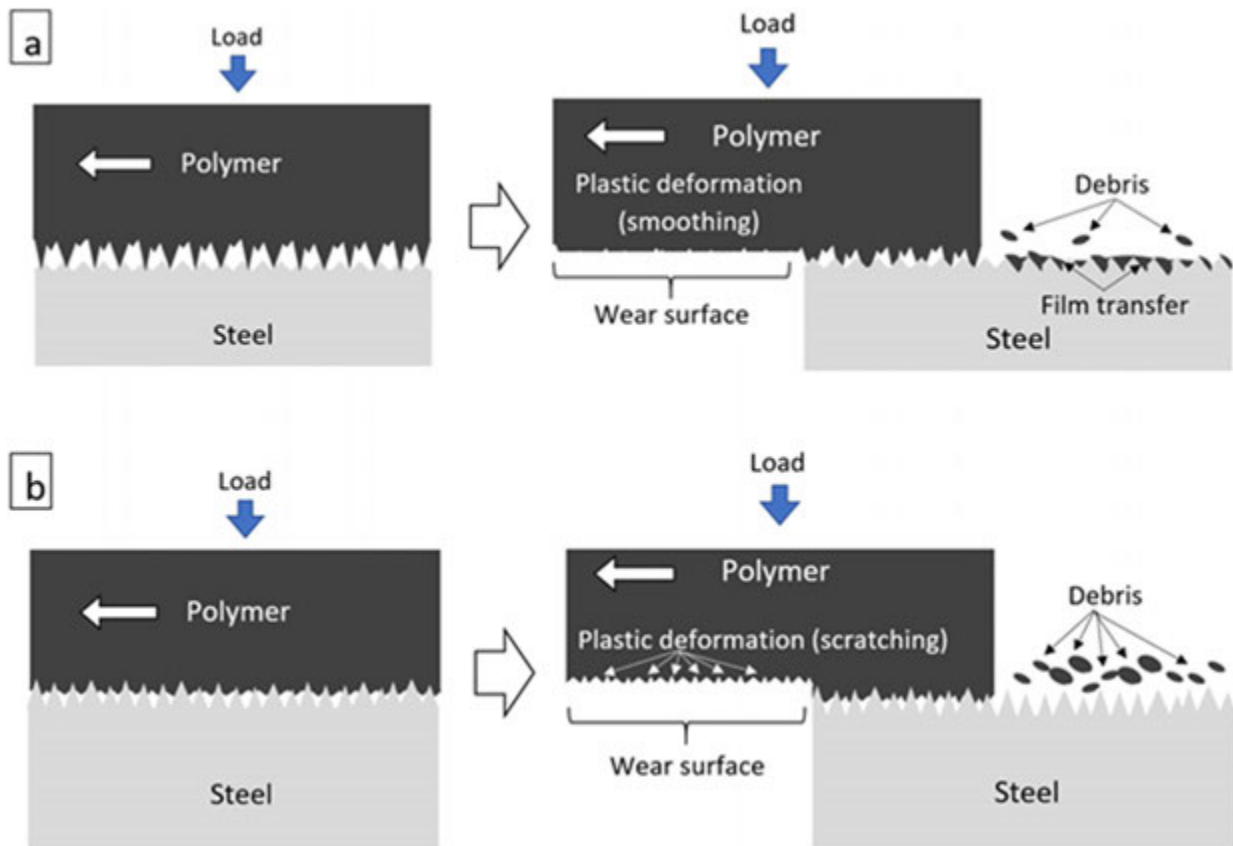


Fig. 4 Schematic representation of wear processes occurred in polymers against metallic surfaces; (a) interfacial wear; (b) cohesive wear.

Classification of Polymer Matrix Composites for Automotive Tribological Applications

PMCs can be overall classified according to its composition and structural architecture (Friedrich *et al.*, 2011). They are made of a polymer matrix, which can be thermo-set, thermoplastic or elastomer, and reinforcements of a non-polymer material, the most typical being glass, carbon, aramid, natural, ceramics, etc. The reinforcement material, with continuous or discontinuous architectures may be arranged in specific order into the matrix. Depending on the architecture, matrix and reinforcement materials, different physical and chemical properties are conferred to the composites. Those composites exhibiting suitable friction, wear or lubricating properties are sub-classified, according to their application, as tribological PMCs. Apart from appropriate tribological properties, they can be designed to achieve other characteristics required to meet specific applications and exhibit enhanced performance as tribo-components (Friedrich, 2018). Therefore, tribological PMCs can be divided into self-lubricating, friction, electrically conductive, high or low temperature resistant and self-healing as shown in Fig. 5. The attributes of each of these materials have fostered development of improved products and components for the automotive industry. The description of each category and some actual examples are given in the subsequent sections.

Self-Lubricating Composites

Self-lubricating PMCs are materials created to reduce friction and wear in tribological components that may experience lubricant starvation during its operation or when the use of lubricants is not recommended. They are two-phase systems, namely, a soft phase made of a lubricant reinforcement and the polymer matrix as the hard phase (Friedrich, 2018). The main attributes of self-lubricating composites are low-noise operation over a long period of time, low shear strength in the sliding direction, high compression strength in the load direction, and low COF throughout the entire service life of the component (Sorrentino, 2018). The most common examples of automotive components for this type of composites are rolling bearings, door hinges, sliding bearings, shock absorbers and bushings of steering shaft joints and windshield wipers. Bushings are used to absorb road bumps, control the movement in the joints and reduce noise and vibration.

The composite materials for these bushings are also used as bearings or coatings for bearings in high pressure and diesel fuel injection pumps. One formulation approach for these is the polyetheretherketone plastic matrix compounded with special micro- and nano-scaled fillers to improve its tribological properties (Friedrich, 2018). On the other hand, an example of a proprietary

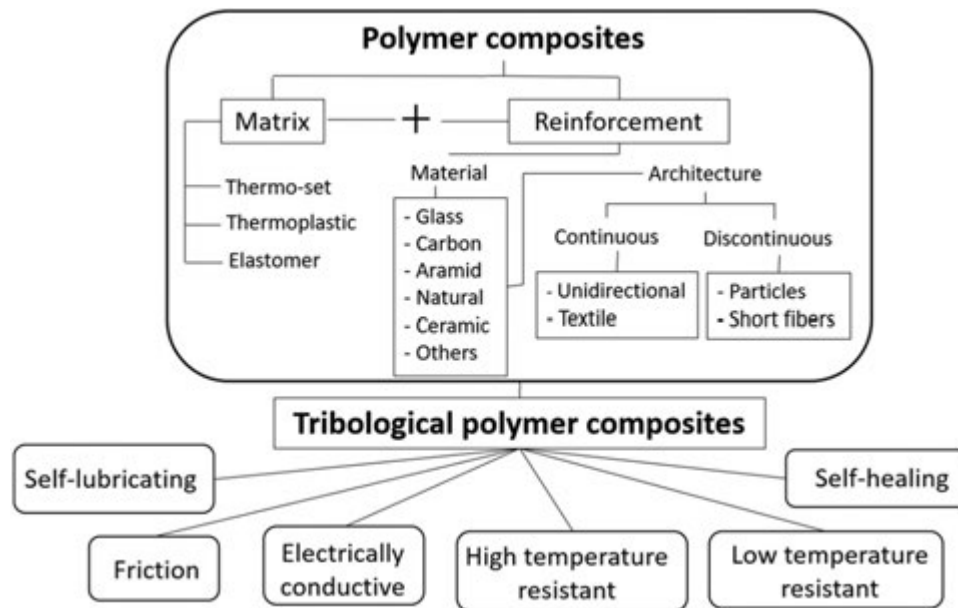


Fig. 5 Classification of polymer matrix composites and subclasses of tribological PMCs for automotive applications.

high performance polyimide resin (Polyamide P84®NT by EVONIK) is commercially available as a fine powder, which can be blended with solid lubricants such as graphite, molybdenum disulfide, or polytetrafluoroethylene to make self-lubricating components as bushings, seals, bearings components, guides, and gear wheels in the automotive industry (EVONIK Industries, 2011).

Natural fibers have also been investigated as potential reinforcements in self-lubricating composites. For example, polyester reinforced with kenaf particles has been found to exhibit non-abrasiveness during processing in a wear rate test. The layer transfer mechanism works at high loads and provides a significant reduction of wear and friction (Nordin *et al.*, 2013). Palm kernel activated carbon epoxy composite is another potential self-lubricating composite. It has the capability to reduce its wear rate and friction coefficient for increasing applied load and different temperatures (Mohmad *et al.*, 2018).

Friction Composites

Friction composites are materials used to generate high and stable friction. Properties of this sort of composites contrast with most desirable characteristics of all other tribological PMCs categories, in which friction reduction to a large extent is desirable. Additionally, friction composites must possess good thermal conductivity, excellent heat and wear resistances, good compatibility or weak absorbability of water, oil and brake fluids, as well as reduced propensity to produce shudder, noises and harshness (Cox, 2012). The most common applications of this type of materials in vehicles are brakes, clutches, belts and tires. Brakes use friction to decrease speed of the vehicle meanwhile clutches, belts and tires use friction to control power transmission and/or traction. The most common polymeric matrixes for brakes and clutches are made of thermosetting polymers (i.e., epoxy and phenolic) while the main reinforcements are fibers, binders, friction modifiers and fillers (Biczko *et al.*, 2017). Fibers of aramid, glass, carbon and steel are the most typically used (Briscoe and Sinha, 2008). In the case of tires and belts, they are widely made of rubber or elastomers. So, various rubber composites reinforced with fibers are being developed for enhanced performance (Visakh *et al.*, 2013). For example, tires are made of a rubber composite (raw rubber with sulfur and carbon black) and steel cords or organic fibers. The rubber, which can be neoprene, natural rubber, styrene-butadiene rubber, nitrile, etc., provides the friction required for traction while the steel cord or organic fiber provides the mechanical strength required to support the load or pressure and impacts (Ikeda *et al.*, 2018).

An important fact to consider during operation of friction materials are wear debris of different chemistries, which are toxic or show mutagenicity, that are released into the environment. So, using natural and non-toxic materials is a current trend for developing environmentally friendly materials for this application. Since asbestos were barred as a constituent to produce friction composites in 1980's due to its adverse effect on human health, several substitutes so-called "green composites" have been investigated and developed (Matějka *et al.*, 2013). For example, cellulose based fibers and plant fibers, namely, kenaf, betelnut, sisal, jute, flax, sugarcane, bamboo, etc., as well as powders of nut shells, coconut shells, hazelnut shells and palm kernel shells are being studied as potential reinforcements in friction composites (Dadkar *et al.*, 2009; Matějka *et al.*, 2013). In the case of tires, some of the most recent and successful improvements of tribological performance of elastomer composites is based on nanotechnology. For this, a series of nanoparticles, namely, silica, core/shell polymer, poly(alkylbenzene)-poly(diene), polyhedral oligomeric silsesquioxanes, carbon nanotubes, graphene, aerogels, nano-diamond and fullerenes have been used as reinforcements for the rubber matrixes (Keams and

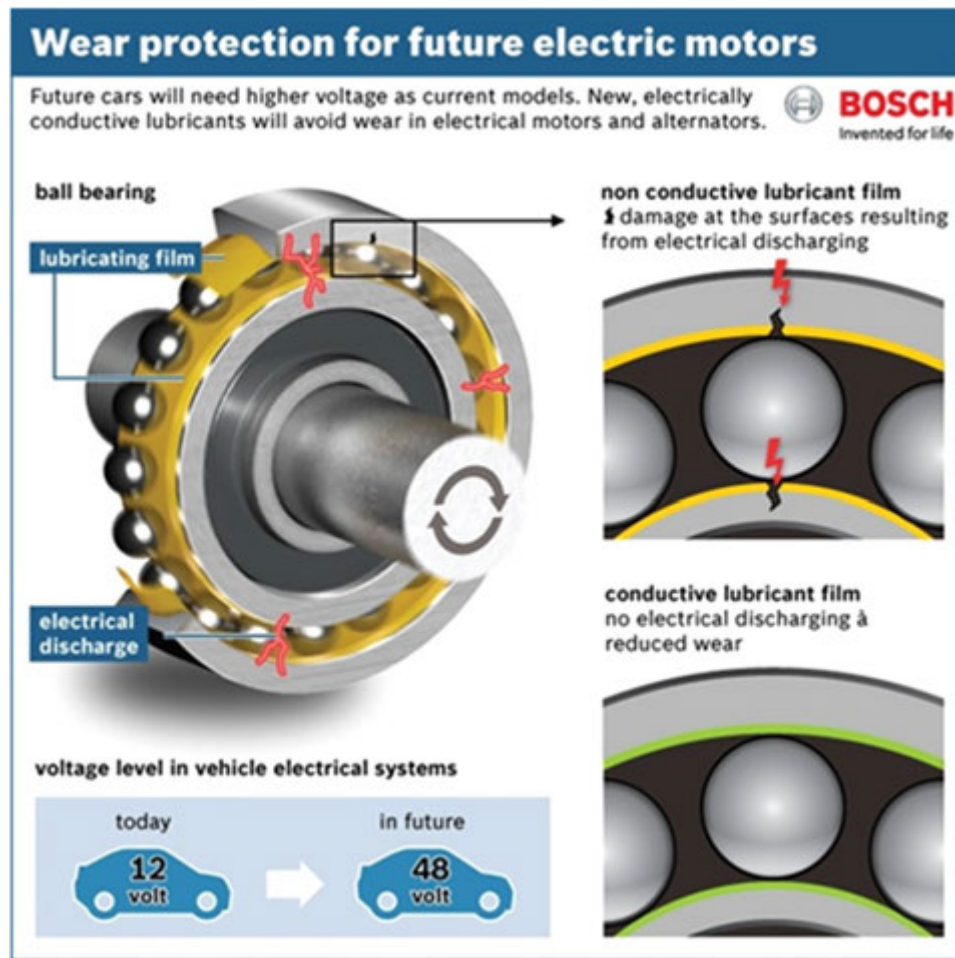


Fig. 6 Diagram of a conductive bearing for electrified vehicles. Reproduced from Bosch, R., 2014. Conductive Lubricants Will Protect the Electric Motors of the Future. Available at: <https://www.bosch-presse.de/pressportal/de/en/conductive-lubricants-will-protect-the-electric-motors-of-the-future-42628.html> [last access: july 2020].

Baucher, 2014). The purposes of using these nanomaterials is to enhance curing as well as mechanical and dynamic mechanical properties which result in improved processability and reduced hysteresis, vehicle fuel consumption and cost. For example, the cluster-like physical structure of silica particles is suitable to arrest crack propagation during tearing by introducing tortuosity in its path, which results in higher tearing energy for crack propagation. So, silica particles may help for crack arresting during tearing, fatigue and possibly wear in a tire tread compound (Veiga *et al.*, 2017).

Electrically Conductive Composites

Tribological conducting PMCs are materials that have good friction and wear characteristics along with a certain electrical conductivity. The most common composites meeting these properties are engineering and specialty polymers reinforced with traditional fillers of intrinsically high electrical conductivity, as carbon nanofibers, multiwall carbon nanotubes, short graphite fibers, etc. (Friedrich, 2018). This type of composites offers ample possibilities for automotive applications, since combine the intrinsic properties of polymers, namely, low density, corrosion resistance and toughness with those of the reinforcements, as wear resistance, stiffness, strengths and electrical conductivity.

Conductive bearings for electro-coating processes in automotive industry, conductive ball cages and greases for bearings (Friedrich, 2018), and conductive dynamic seals for electric vehicle powertrains are the most important automotive applications of these composites (BioAge Group, 2019; Farfan-Cabrera, 2019). For example, an electrocoating process for painting vehicles requires all the components of the assembly to be electrically conductive for better performance. This helps to accelerate the painting process by facilitating attraction and deposition of painting particles in the car body and produce a continuous film over every surface until the coating reaches the desired thickness (Friedrich, 2018). In the case of conductive bearings, greases and dynamic seals, they are developed to avoid failures in electric motors and transmissions due to surface damage or wear caused by electrical discharges. This phenomenon, illustrated in Fig. 6, and technically known as electrical discharge machining or spark



Fig. 7 Dry film lubricant coatings on the head of the piston (slick lubricant). Reproduced from JCM Automotive Machine Shop and Coatings, 2011. Available at: www.jcmmachineandcoatings.com. [online] Available at: <https://www.jcmmachineandcoatings.com/coatings/pistons/> [last access: July 2020].

machining, is a problem in electrified powertrains. At present, electric vehicles operate with 12 volts to provide all conventional automotive electric systems with enough power. This voltage, however, may change to 48 volts to support a growing number of functions in vehicles in next few years. Higher levels of voltage will result in stronger alternating electric fields in alternators and electric motors causing electrical discharge in the ball bearings. Produced sparks can melt tiny areas of the metal's surface generating irregular raceways, and consequently, noise and premature failures. So, bearings and seals should be electrically conductive (Bosch, 2014). Conventional seals are made of insulating polymeric materials and are not suited for this purpose. Hence, new conductive seals made of elastomer matrix with special conductive fibers are being developed (BioAge Group, 2019). As for conductive greases, these are formulated with a high percentage of conductive powder of various natures, conveyed in synthetic oils/silicone. Another example is a gel-based polyester thickened with carbon black. The fundamental characteristics of these greases are their low volatility, high thermal stability at high temperatures, high spread ability and electrical conductivity (Technolube-Seal, 2017).

High-Temperature Resistant Composites

High-temperature resistant PMCs are materials able to operate at elevated temperature while keeping their tribological properties. This sort of composites, qualified to provide dimensional stability and long-term durability when exposed to hot environments, consist of a polymer matrix with high T_g and reinforcements with flame retardancy. Typical matrix polymers for this application are thermosets, as epoxy and thermosetting polyamides, and thermoplastics, as polyimides and polyarylene ethers, such as polyetheretherketone and polyethersulfone; meanwhile reinforcements may be of continuous aligned, glass, carbon or ceramic fibers. Short fibers and whiskers are not often used for this application, although enhanced tribological behavior has been reported for polyetheretherketone and polyetherimide reinforced with short carbon fibers, graphite flakes, and sub-micro particles of TiO_2 and ZnS under dry sliding (Chang *et al.*, 2007).

The highest temperature in a vehicle takes place inside the engine, affecting tribological components such as the crankshaft bearings and pistons, which may reach temperatures up to around 300°C. Conventional aluminum alloys can cope with this requirement, but request for lighter materials opens a novel possibility for polymer composites. New high-temperature resistant composites are being used for coatings of such bearings and pistons (see Fig. 7). Currently, there are various polymeric candidates suitable as matrices for coatings in these applications, examples of these are polyethersulfone that possess a service temperature above 290°C and excellent corrosion resistance, polytetrafluoroethylene and perfluoroalkoxy alkanes which have a service temperature about 260°C, low COF and high wear resistance (Pei *et al.*, 2016). In addition, polytetrafluoroethylene has self-lubricating properties (Myshkin *et al.*, 2015), which make it suitable as matrix or reinforcement (Chaudhari, 2013). Polybenzimidazole is of great interest for companies due to its excellent thermal, mechanical and tribological properties (Tanaka *et al.*, 2006), with good wear resistance, excellent substrate adhesion and high fatigue resistance (Samad and Sinha, 2010). Polyamideimide, also named as Torlon from Solvay S.A., company, is compounded with solid lubricants as MoS_2 or graphite to improve the tribological behavior for piston coatings and crank shaft bearings. Another example is the aforementioned polyimide resin (Polyimide P84NT®), which has a high T_g and high deflection temperature, making it appropriate for high-temperature composites.

The DSM company (Evansville, Ind.) developed a polyphthalamide with glass transition temperature up to 160°C, the commercial name is Stanyl ForTii®. It is a composite with several grades up to 60% of glass fiber content (DSM, 2018). The high

polymer crystallinity of Stanyl ForTii® provides excellent wear-resistance and has been used in thrust bearings, bushings, chain guides and timing chains of vehicles at operating temperatures up to 180°C (Legault, 2012).

Within the bioplastics currently available on the market, some materials are already validated for high-temperature applications. The bio-based polyamides exhibit good properties, namely, high wear resistance, good heat resistance, chemical resistance to oils and solvents, and fire resistance (Kohan *et al.*, 2003), which make them suitable for under-the-hood components such as air cleaner, throttle valve guards and throttle valves in automobile engines. Several bio-based PA's, which are derived from renewable feedstocks, such as castor beans and sugar cane, have also appeared on the market. The automotive applications of these commercial bio- polyamides and their glass-fiber composites also include charge air duct for engines. Rilsa-® HT Polyamide 11 from Arkema, for instance, is used in the exhaust gas recirculation tubes instead of those made of metallic materials, such as aluminum, for Peugeot and Citroën vehicles (French cars brands of Groupe PSA) (Arkema Group, 2009).

Low-Temperature Resistant Composites

Low-temperature resistant PMCs are materials able to operate at cryogenic temperatures ($< 150^{\circ}\text{C}$) while keeping their tribological properties. To have a proper tribological performance under this extreme environment, these composites should possess good heat dissipation or high heat conductivity, specially at the sliding contact regions, the matrix and reinforcements must have similar thermal expansion coefficients to limit thermal stresses in the boundary surfaces of the components, low chemical reactivity with cryogenic fluids and ductility at low temperatures. In general, the friction coefficient of polymer matrix composites can be reduced, even at low temperatures, by increasing their thermal conductivity (Friedrich, 2018). The most promising candidates for this purpose are polytetrafluoroethylene and polyetheretherketone composites, since they have been successfully used in other cryogenic applications as in rockets (Fusaro, 1990; Theiler and Gradt, 2013). They present outstanding tribological properties in both, room and low temperatures. The most common reinforcements used for these composites are glass and carbon fibers.

The development of new applications of cryotechnology in the automotive industry is underway, for example, in superconductors for zero friction bearings (Mukoyama *et al.*, 2017) and zero emissions hydrogen combustion engines (Gurz *et al.*, 2017). The use of this technology requires materials able to withstand cryogenic temperature and exposure to extreme environments with helium, cryogenic liquids or vacuum without losing performance (Friedrich, 2013). The most critical tribo-components in hydrogen combustion vehicles are bearings, dynamic seals and valves for pump and injectors. Also, external tribological hardware having high-performance in cryogenic environment, namely, pumps, valves and seals, is required for refueling, servicing and maintenance processes of such vehicles (Gurz *et al.*, 2017). The temperature existing in hydrogen engines is significantly lower than in gasoline or diesel internal combustion engines. So, most semi-crystalline polymers could be also used to substitute different tribological parts into the hydrogen engine, which are not subjected to cryogenic temperatures, but to lower temperatures than those of gasoline or diesel combustion engines (Stead *et al.*, 2019). Considering that conventional lubricants are not recommended to be used at cryogenic temperatures, self-lubricating polymers and composites are considered as the future trend for producing low-temperature resistant PMCs.

Self-Healing Composites

Self-healing PMCs are materials that may recover their properties after damage, without external intervention. The most popular application of this kind of composites is in automotive paint coatings. The term “coating” implies any thin layer covering another material. The protective function of the coating is related to the underlying substrate (automobile metal body), it must be sealed off from external environment such as light, humidity, air, dirt, chemicals, mechanical abrasion and corrosion. The coating damage can be seen as the immediate loss of its protective function induced mainly by internal microcracking, which dramatically truncates the lifetime of the coated structures. The detection and repair of the inside damages in the materials was relatively impossible till the discovering of self-healing materials. They are made by the embodiment of encapsulated or enclosed micro- or nano-sized healing agents into a polymer matrix. It is to isolate and protect the agents from the external environment (Kanu *et al.*, 2019). The healing mechanism starts when the enclosed micro/nano capsules in the host material break and cause releasing of the healing agents through the generated cracks by capillary phenomena. Then, the released healing agent solidifies by a polymerization reaction with the active materials inducing polymerization in the host matrix. Also, it cures after reacting with the already embedded catalyst or with oxygen to seal the created cracks (Ataei *et al.*, 2019). One relevant example of a composite exhibiting outstanding self-healing properties is the epoxy resin enclosing encapsulated dicyclopentadiene and Grubb's enzymes. When dicyclopentadiene associates with the Grubbs' enzymes, which is diffused in the epoxy resin, a ring like opening metathesis polymerization is initiated and a cross-linked tough polycyclopentadiene is thereafter formed to heal the damage (Kanu *et al.*, 2019). Apart from dicyclopentadiene and Grubb's enzymes, other materials have been demonstrated as healing agents for epoxy resins, for example, epoxy and amine, mercaptan, phenylacetate, ethyl phenyl acetate, chlorobenzene, linseed oil, tung oil and alkyd resins (Ataei *et al.*, 2019; Adekunle, 2015; Suryanarayana *et al.*, 2008). Regarding developments and applications of self-healing composites in the automotive industry, the Nissan Motor Co. Ltd developed a paint coating with the potential of self-healing upon exposure to wear and several chemical media (Bentham *et al.*, 2007). This material is based on epoxy resins with high thermo-mechanical performance, excellent adhesion, good chemical resistance, and corrosion resistance. The recovery time has a close relationship with the depth of the scratch and temperature in the surrounding environment.

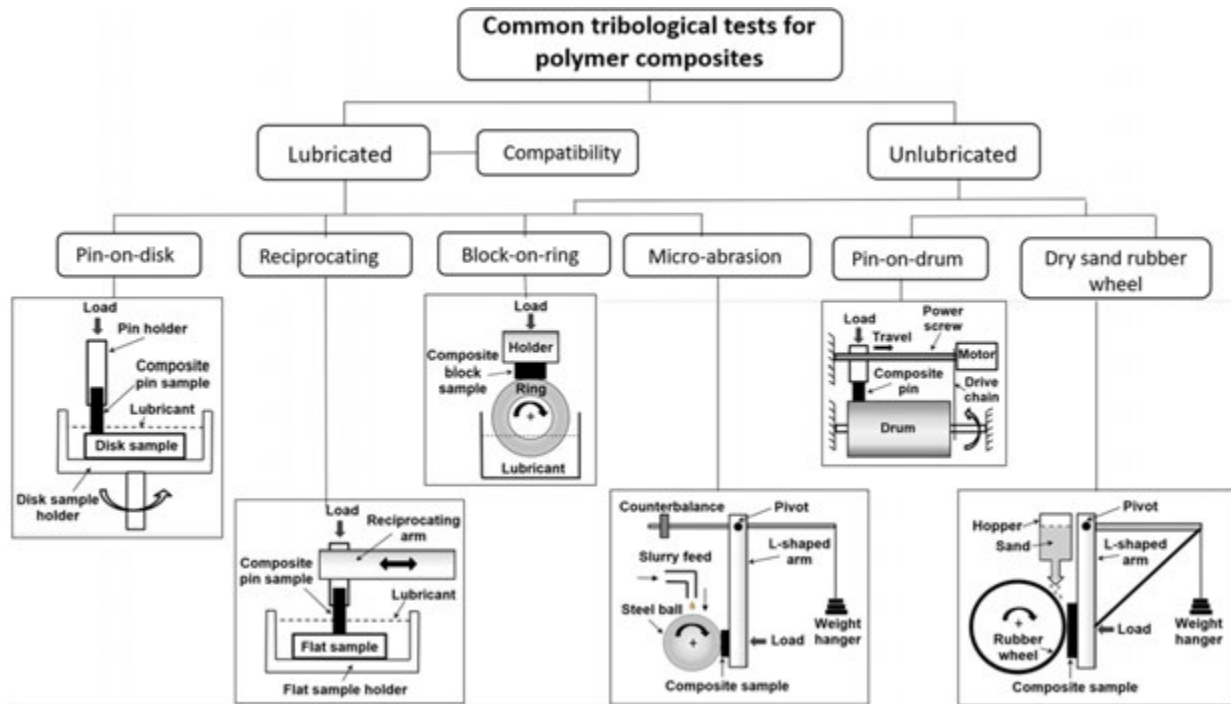


Fig. 8 Typical tribological tests for evaluating PMCs.

Typical Tribological Tests for Automotive Polymer Matrix Composites

The definitive evaluation of PMCs to give them reliable tribological applications require their full-scale testing in situ, where entire components are subjected to actual operating environments. In such a way, accurate assessment of useful life and tribological performance can be determined. This, however, may be excessively expensive and time-consuming, so most researchers and manufacturers prefer less complex tribological testers to approach realistic critical wear and friction conditions. Thus, the friction and wear behavior of polymer matrix composites for automotive tribological components can be evaluated by several short and low-cost tribological tests. The most common tribological tests are illustrated in Fig. 8, they can be conducted under dry or lubricated conditions depending on the specific application of the material. The pin-on-disk, reciprocating, block-on-ring, micro-abrasion, pin-on-drum and dry sand rubber wheel testers can be used for unlubricated tests, while the first four are often used for both lubricated and unlubricated tests. Each tester is capable to reproduce certain controlled tribological conditions, namely, lubrication type, sliding motion and distance, applied load, speed, abrasive environment, temperature, etc., generating measurable wear losses in the tested materials and, in most cases, providing COF measurement. Hence, selecting the most suitable test for evaluating PMCs for tribological applications is crucial for achieving the most realistic approach. A brief description of the aforementioned tribological tests is given below.

Pin-on-Disk Test

The pin-on-disk is considered as one of the most common test for friction and wear characterization of materials due to its low complexity and the capability to reproduce a wide range of lubricated and unlubricated automotive tribo-contacts, such as those of brakes, dry and wet clutches and sliding bearings. The standard configuration of this device allows testing of PMCs under unidirectional sliding, but most modern devices enable testing of materials under other different sliding motion modes including bidirectional and fretting, at controlled speed, time, temperature, humidity, vacuum or load. The test's name comes from the type/geometry of specimens promoting the tribo-contact. In this case, one specimen is a pin that can be flat or spherical (ball) while the other is a disk. Usually, the pin is fixed to an arm that is weighted down onto the disk sample with a certain load. The disk sample is rotated at a controlled and predefined speed. The arm and the pin fixation allow alignment and stable position in the friction track formed by the pin on the disk. The friction force generated by sliding of the pin on disk can be measured and recorded by load or torque sensors installed in the machine. Wear rates can be estimated for both, the pin and the disk, by measuring the weight loss and/or wear volume generated during the test. Pins made of the polymer composite and metallic disks are the typical type of samples tested using this machine. ASTM G99, ASTM F732 and ISO 7148-2 are examples of standard methods suggested for evaluating wear and COF of polymers.

Linear Reciprocating Test

The linear reciprocating tribometer was developed to evaluate the tribological properties of bulk materials, coatings, lubricants and additives which are to be subjected to a reciprocating sliding in their actual application. It allows determination of wear rate and COF of PMCs in lubricated or unlubricated contacts in a wide range of operating conditions, such as load, temperature, frequency and stroke length. Most modern testers can reproduce fretting wear conditions, extreme environments and larger amplitude linear sliding conditions. In general, it can accommodate a variety of sample geometries to create point, line and area contacts being mainly suitable for automotive tribo-components, namely, piston/cylinder liner, shock absorbers, ball joints, etc. The test can be configured in a ball-on-plate or pin-on-plate arrangements. Both consist on positioning a ball or pin perpendicular to the plate and apply a predefined load against the plate. Either the pin or the plate is moved in a linear reciprocating way at a fixed frequency. Friction force is measured during the test via a load cell installed in the tester. Wear rates can be estimated for the pin and the plate by measuring weight loss and/or wear volume generated during the test. Either pins or plates made of the PMC can be prepared and tested using this machine. ASTM G133, ASTM F732 and ISO 19291 are the typical standard methods used to determine wear rate and COF of polymers under reciprocating sliding.

Block-on-Ring Test

The block-on-ring test is a simple method commonly used to assess the tribological behavior of a wide range of solid materials, including PMCs under different sliding conditions and environments, namely, time or sliding distance, load, speed, temperature, humidity and lubrication. Basically, it consists on loading a block, which is usually made of the PMC to be tested, against a rotating metallic ring with a predefined load. Since lubricated and unlubricated tests can be performed in this device, the common automotive tribo-contacts approached by using this tester are those present in sliding bearings and brakes where the predominant wear patterns are produced primarily by abrasion. The frictional force generated by the sliding between the block and ring samples is measured and acquired via a load cell installed in the tester, meanwhile the wear rate of either the block or ring is estimated by measuring the material mass or volume loss generated during the test. The ASTM G77 and ISO 7148-1 procedures are the typical standard methods to perform this test.

Micro-Abrasion Test

The micro-abrasion wear test is a method relatively new for characterization of wear rate and resistance of a wide range of materials, namely, ceramics, metals, coatings, polymers and PMCs. The test is suitable for materials used in automotive components subjected mainly to mechanisms of rolling and grooving abrasion, for instance, dynamic seals, ball joints, paint coatings and journal bearings. The method was introduced by Rutherford and Hutchings in 1997 ([Rutherford and Hutchings, 1997](#)), thereafter, a significant amount of work has been done to improve the test reproducibility and to implement it as a standard wear test for tribological materials ([Gee et al., 2005](#)). The aim of the test is to generate a small wear crater with ellipsoid or spherical cap geometry and defined wear patterns (micro-indentations and/or grooves) on small and thin flat specimens. In the test, regularly, a 25.4 mm rotary ball, which can be made of steel, stainless steel, ceramics or polymers, is loaded against the PMC sample at a predefined load, speed and ball cycles while a slurry containing abrasive micro-particles is supplied at the contact. The typical slurry used for this test is made of silicon carbide (SiC) micro-sized and angular particles (4–8 μm) dispersed in distilled water at a concentration of 80 gr/100 ml. However, other abrasives, namely, silica sand, aluminum oxide (Al_2O_3), sodium bicarbonate (NaHCO_3), glass, etc., can be used. Ball rotation speed and cycles, load, slurry feed flux and concentration can be varied depending on the tribo-contact to be replicated. In up-graded micro-abrasion testers, lubricated conditions can be also reproduced, and COF can be measured during the test by additional sensors installed in the device.

Pin-on-Drum Test

The pin-on-drum test, also known as high-stress abrasive wear, was made to produce and evaluate two-body abrasive wear behavior of bulk materials, including, polymers and PMCs. Basically, one end of a pin specimen is translated linearly over the surface of a rotating drum, which is covered with an abrasive paper usually made of Al_2O_3 , SiC, or garnet of the desired size at a predefined load. During the test, the pin sample is abraded constantly by the sliding within the abrasive paper. The wear is believed to simulate severe abrasive wear that can occur, for example, during rolling or slipping of tires against pavement or other abrasive floors. Parameters as abrasive material and size, pin specimen load and speed, path length and drum rotary speed can be varied in this test. The wear rate is typically estimated by measuring the mass loss of the pin specimen. The measurement of friction is not common in these testers.

Dry Sand Rubber Wheel Test

Severe three-body abrasion wear resistance of metals, ceramics, polymers and PMCs is widely evaluated by the dry sand rubber wheel test. Usually, a flat and robust block specimen is positioned vertically and loaded against the rim of a rotating rubber wheel while sand or other abrasive particles are fed into the gap between the rubber and specimen interface. The abrasive particles act as

the third-body abrader in the contact. The rubber helps the particles to slide against the block specimen consistently. This test is also known as low stress scratching abrasion test. Rolling and slipping of tires in the presence of sand or other abrasive particles can be replicated and evaluated with this test. Different loads, abrasive particles types and sizes, wheel speed and environmental conditions can be tested. The ASTM G65 and ISO 28080 are the typical standard methods based on the dry sand rubber wheel test. In general, they are focused on determining the wear rate and resistance of materials while friction measurement is not considered.

To end up this section, it is noteworthy that in the case of lubricated tests for PMCs, additional compatibility tests should be carried out since it is well known that certain polymers, depending on their polarities, may be incompatible with different solvents or lubricants (Farfan-Cabrera *et al.*, 2019). Incompatibility promotes accelerated degradation of the polymer in the solvent (i.e., automotive lubricants and combustibles) producing dissolution, swelling and/or hardening and loss of resilience (Farfan-Cabrera *et al.*, 2017a, 2018).

Automotive lubrication systems comprising PMCs components require good compatibility with lubricants to avoid failures due to degradation by incompatibility. Thus, novel developed PMCs should be compatible with most of the common lubricants used for the specific tribological application. Currently, there are not established standard tests for determining compatibility of polymer matrix composites with lubricants in different environmental conditions, but some standard tests for polymers compatibility, namely, ASTM-D471, ASTM-D7216, ASTM-D4289, ASTM D543, ISO 6072, ISO 175, etc., can be used. Basically, the procedures consist on conducting immersion tests of the polymers in the chemical fluid aimed under specific conditions, and then, measuring changes of their physical properties after a precise immersion period. The typical measured properties are mass, volume, hardness, tensile and tear strength, elongation, breaking resistance, burst strength, etc. The compatibility level is stated depending on the changes occurred after immersion.

Prospective Developments and Challenges

Automotive industry will continue demanding high-performance materials, including tribological PMCs. They should be able to sustain higher pressures, temperatures and velocities while being partially or totally eco-friendly. The emerging area of polymer nanocomposites offers expectative for achieving significant advances. The main advantage of nanocomposites over traditional PMCs is the ability of the former to improve both strength and toughness properties simultaneously and isotropically (Briscoe and Sinha, 2008). Considering that research and development of tribology of nanocomposites and hybrid composites is still scarce, but growing, many innovations in the automotive technology, even in new high-performance hardware, namely, micro- and nano-electro-mechanical systems (MEMS and NEMS), for electric vehicles will appear in the coming years (Friedrich, 2013; Farfan-Cabrera, 2019). Finally, the tribological application of PMCs is expected to grow as the usage of polymers expands to newer applications in vehicles. Since polymers do not always follow the rule of better strength and hardness for better wear resistance and desired COF, there will be always a need for fine-tuning tribological performances of the material without seriously compromising the bulk strength. Thus, a healthy rise in the research area of tribological PMCs is expected (Briscoe and Sinha, 2008).

References

- Adekunle, K.F., 2015. A review of vegetable oil-based polymers: Synthesis and applications. *Open Journal of Polymer Chemistry* 5 (3), 34–40.
- Aldousiri, B., Shalwan, A., Chin, C.W., 2013. A review on tribological behaviour of polymeric composites and future reinforcements. *Advances in Material Science and Engineering*, 1–8. (645923).
- American Chemistry Council, 2019. [www.automotiveplastics.com](https://www.automotiveplastics.com/wp-content/uploads/Plastics-and-Polymer-Composites-in-Light-Vehicles-2019-REV-Sm.pdf). [online] Available at: <https://www.automotiveplastics.com/wp-content/uploads/Plastics-and-Polymer-Composites-in-Light-Vehicles-2019-REV-Sm.pdf> [last access: July 2020].
- Arkema Group, 2009. [www.arkema.com](https://www.arkema.com/en/media/news/news-details/Rilsan-HT-the-first-flexible-high-temperature-thermoplastic-to-replace-metal-in-engine-compartment-tubing). [online] Available at: <https://www.arkema.com/en/media/news/news-details/Rilsan-HT-the-first-flexible-high-temperature-thermoplastic-to-replace-metal-in-engine-compartment-tubing> [Last access: July 2020].
- Ataei, S., Khorasani, S.N., Neisiany, R.E., 2019. Biofriendly vegetable oil healing agents used for developing self-healing coatings: A review. *Progress in Organic Coatings* 129, 77–95.
- Benthem, V.R.A.T.M., Ming, W., With, G.D., 2007. Self healing polymer coatings. In *Self Healing Materials*. Berlin: Springer, pp. 139–159.
- Biczó, R., Kalácska, G., Szakál, Z., Fledrich, G., 2017. Composite friction materials for brakes and clutches. *Scientific Bulletin, Series C, Fascicle: Mechanics, Tribology, Machine Manufacturing Technology* 2016, 21–26.
- BioAge Group, 2019. Green Car Congress: Energy, Technologies, Issues and Policies for Sustainable Mobility. [online] Available at: <https://www.greencarcongress.com/newsletter-subscription.html> [last access: July 2020].
- Bosch, R., 2014. Conductive Lubricants Will Protect the Electric Motors of the Future. Available at: <https://www.bosch-presse.de/pressportal/de/en/conductive-lubricants-will-protect-the-electric-motors-of-the-future-42628.html> [last access: July 2020].
- Briscoe, B.J., Sinha, S.K., 2005. Tribology of polymeric solids and their composites. In: Stachowiak, G.W. (Ed.), *Wear - Materials, Mechanisms and Practice*. Wiley, pp. 223–267.
- Briscoe, B.J., Sinha, S.K., 2008. Chapter 1 – Tribological applications of polymers and their composites: past, present and future prospects. In: Friedrich, K., Schlarb, A.K. (Eds.), *Tribology of Polymeric Nanocomposites: Friction and Wear of Bulk Materials and Coatings*, vol. 55. Elsevier, pp. 1–14.
- Chang, L., Zhang, Z., Ye, L., Friedrich, K., 2007. Tribological properties of high temperature resistant polymer composites with fine particles. *Tribology International* 40 (7), 1170–1178.
- Chaudhari, S., 2013. Wear Analysis of Polytetrafluoroethylene (PTFE) and its Composites under Wet Conditions. *IOSR Journal of Mechanical and Civil Engineering* 8 (2), 7–18.
- Cox, R., 2012. *Engineered Tribological Composites: The Art of Friction Material Development*. Warrendale, PA: SAE International.

- Dadkar, N., Tomar, B.S., Satapathy, B.K., 2009. Evaluation of flyash-filled and aramid fibre reinforced hybrid polymer matrix composites (PMC) for friction braking applications. *Materials & Design* 30 (10), 4369–4376.
- DSM, 2018. www.dsm.com/markets/engineering-materials/en/products/fortii.html [last access: July 2020].
- EVONIK Industries, 2011. www.p84.com/sites/lists/re/documentshp/evonik-polyimide-p84nt-technical-brochure.pdf [last access: July 2020].
- Farfan-Cabrera, L., Gallardo-Hernández, E., Pérez-González, J., 2017a. Compatibility study of common sealing elastomers with a biolubricant (Jatropha oil). *Tribology International* 116, 1–8.
- Farfan Cabrera, L.I., Gallardo Hernández, E.A., Sedano de la Rosa, C., Vite Torres, M., 2017b. Micro-scale abrasive wear of some sealing elastomers. *Wear* 376, 1347–1355.
- Farfan-Cabrera, L., Pérez-González, J., Gallardo-Hernández, E., 2018. Deterioration of seals of automotive fuel systems upon exposure to straight jatropha oil and diesel. *Renewable Energy* 127, 125–133.
- Farfan-Cabrera, L.I., 2019. Tribology of electric vehicles: A review of critical components, current state and future improvement trends. *Tribology International* 138, 473–486.
- Farfan-Cabrera, L.I., Pérez-González, J., Gallardo, E., 2019. Solubility analysis of elastomers in a bio-based lubricant using Hansen parameters. *Materials Research Express* 6 (1), 015311.
- Fox, M., 2016. Lube-Tech. [online] Available at: <http://www.lube-media.com/wp-content/uploads/2017/11/Lube-Tech106-PolymerTribology.pdf> [last access: July 2020].
- Friedrich, K., 1997. *Wear Performance of High Temperature Polymers and Their Composites*. Boca Raton: Taylor & Francis Group CRC Press.
- Friedrich, K., 2013. Polymers for low-temperature tribology applications. In: Jane Wang, Q., Chung, Y.-W. (Eds.), *Encyclopedia of Tribology*. Boston, MA: Springer.
- Friedrich, K., 2018. Polymer composites for tribological applications. *Advanced Industrial and Engineering Polymer Research* 1 (1), 3–39.
- Friedrich, K., Lu, Z., Hager, A.M., 1995. Recent advances in polymer composites' tribology. *Wear* 190 (2), 139–144.
- Friedrich, K., Chang, L., Hauptert, F., 2011. Current and future applications of polymer composites in the field of tribology. In: Nicolais, L., Meo, M., Milella, E. (Eds.), *Composite Materials*. London: Springer. doi:10.1007/978-0-85729-166-0_6.
- Fusaro, R.L., 1990. Self-lubricating polymer composites and polymer transfer film lubrication for space applications. *Tribology International* 23 (2), 105–122.
- Gee, M.G., *et al.*, 2005. Results from an interlaboratory exercise to validate the micro-scale abrasion test. *Wear* 259 (1–6), 27–35.
- Gurz, M., Baltacioglu, E., Hames, Y., Kaya, K., 2017. The meeting of hydrogen and automotive: A review. *International Journal of Hydrogen Energy* 42 (36), 23334–23346.
- Hutchings, I., Shipway, P., 2017. *Tribology Friction and Wear of Engineering Materials*, second ed. United Kingdom: Elsevier.
- Ikeda, Y., Kato, A., Kohjiya, S., Nakajima, Y., 2018. Pneumatic tire technology. In: Ikeda, Y., Kato, A., Kohjiya, S., Nakajima, Y. (Eds.), *Rubber Science: A Modern Approach*. Singapore: Springer, pp. 155–191.
- Kanu, N., Gupta, E., Vates, U., Singh, G., 2019. Self-healing composites: A state-of-the-art review. *Composites Part A: Applied Science and Manufacturing* 121, 474–486.
- Kazmierski, C., 2012. Lucintel. [online] Available at: <https://www.lucintel.com/lucintel-globalcompositemarketanalysis-acma2012-educationalsession.pdf> [last access: July 2020].
- Kearns, P.W.E., Baucher, M.A., 2014. Nanotechnology and Tyres: Greening Industry and Transport. OECD. Available at: <http://www.oecd.org/env/ehs/nanosafety/nanotechnology-tyres-greening-industry-and-transport.htm>.
- Kohan, M.I., Mestemacher, S.A., Pagilagan, R.U., Redmond, K., 2003. Polyamides. In: Ullmann's Encyclopedia of Industrial Chemistry. s.l.:Wiley-VCH Verlag GmbH & Co. KGaA. pp. 1–47.
- Legault, M., 2012. *Composites World*. [online] Available at: <https://www.compositesworld.com/articles/high-temp-thermoplastics-higher-expectations> [last access: July 2020].
- Matějka, V., *et al.*, 2013. Jute fibers and powdered hazelnut shells as natural fillers in non-asbestos organic non-metallic friction composites. *Materials & Design* 51, 847–853.
- Mohmad, M., *et al.*, 2018. Physical-mechanical properties of palm kernel activated carbon reinforced polymeric composite: potential as a self-lubricating material. *Jurnal Tribologi*. 77–92.
- Mukoyama, S., *et al.*, 2017. Development of superconducting magnetic bearing for 300 kW flywheel energy storage system. *IEEE Transactions on Applied Superconductivity* 27 (4), 1–4.
- Myshkin, N., Pesetskii, S., Grigoriev, A.Y., 2015. Polymer tribology: Current state and applications. *Tribology in Industry* 37 (3), 284–290.
- Nordin, N.A., *et al.*, 2013. Wear rate of natural fibre: Long Kenaf composite. *Procedia Engineering* 68, 145–151.
- Pei, X.-Q., *et al.*, 2016. Tribological synergy of filler components in multifunctional polyimide coatings: Filler components in multifunctional polyimide coatings. *Advanced Engineering Materials* 19 (1), 1600363.
- Reinicke, R., Hauptert, F., Friedrich, K., 1998. On the tribological behaviour of selected, injection moulded thermoplastic composites. *Composites Part A: Applied Science and Manufacturing* 7 (29), 763–771.
- Rutherford, K., Hutchings, I., 1997. Theory and application of a micro-scale abrasive wear test. *Journal of Testing and Evaluation* 25 (2), 250–260.
- Samad, M.A., Sinha, S.K., 2010. Nanocomposite UHMWPE–CNT polymer coatings for boundary lubrication on aluminium substrates. *Tribology Letters* 38 (3), 301–311.
- Shackelford, J.F., Alexander, W., 2014. *Materials Science and Engineering Handbook*, eighth ed. New York Washington: CRC Press LLC.
- Sorrentino, A., 2018. Tribology of self-lubricating polymer nanocomposites. In: Menezes, P.L., Rohatgi, P.K., Omrani, E. (Eds.), *Self-Lubricating Composites*. Switzerland: Springer Nature, pp. 105–131.
- Stead, I.M.N., *et al.*, 2019. Towards a plastic engine: Low-temperature tribology of polymers in reciprocating sliding. *Wear* 430–431, 25–36.
- Suryanarayana, C., Rao, K.C., Kumar, D., 2008. Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings. *Progress in Organic Coatings* 63 (1), 72–78.
- Suschem, 2017. Polymer composites for automotive sustainability. Available at: http://www.suschem.org/files/library/Publications/POLYMERS_Brochure_Web.
- Tanaka, T., *et al.*, 2006. Studies on Lead-free Resin Overlay for Engine Bearings. SAE Technical Paper, Issue No. 2006-01-1104.
- Technolube-Seal, 2017. CONductive or Dissipative Paste. [online] Available at: <http://www.tecnolubeseal.it/products/dissipative-or-conductive-pastes/?Lang=en&langen> [last access: July 2020].
- Theiler, G.E., Gradt, T., 2013. Friction and wear of polymer materials at cryogenic temperatures. In: Kalia, S., Fu, S.-Y. (Eds.), *Polymers at Cryogenic Temperatures*. Berlin, Heidelberg: Springer, pp. 41–58.
- Veiga, V.D., Rossignol, T.M., Crespo, J. d.S., Carli, L.N., 2017. Tire tread compounds with reduced rolling resistance and improved wet grip. *Journal of Applied Polymer Science* 134 (39), 45334.
- Visakh, P.M., Thomas, S., Chandra, A.K., Mathew, A.P., 2013. *Advances in Elastomers I: Blends and Interpenetrating Networks*, first ed. Verlag Berlin Heidelberg: Springer.
- Zhang, S., 1992. Wet abrasion of polymers. *Wear* 158 (1–2), 1–13.

Polymer Matrix Composites Materials for Water and Wastewater Treatment Applications

Maryam Ahmadzadeh Tofighy and Toraj Mohammadi, Iran University of Science and Technology, Tehran, Iran

© 2021 Elsevier Inc. All rights reserved.

Introduction

Only 0.8% of the earth's total water is clean water, which is a vital element for survival of all living things (Nasir *et al.*, 2019). Nowadays, with rapid industries development and increasingly growing world population, the global water shortage problem is becoming more and more serious. Currently, 2 billion people in the world do not have access to clean water, that may reach 4.6 billion by 2080 (Huang *et al.*, 2014). In many developing countries, almost 90% of contaminated water is discharged into environment directly without any treatment. Major sources of water pollution include municipal and industrial wastewater as well as agricultural activities (Nasir *et al.*, 2019). Consumption of contaminated water threatens human health and causes various diseases such as cancer, wounds, skin inflammations, diarrhea, fever and chills, headache and abdominal pain and loss of appetite (Dongre *et al.*, 2019). Therefore, providing clean water from limited water resources and removing contaminants from water/wastewater are very important. Among water pollutants, heavy metal ions and dyes are the most harmful (Qu *et al.*, 2012; Yang *et al.*, 2018; Teow and Mohammad, 2019).

Wastewater from many industries including battery manufacturing, chemical manufacturing, metallurgical, tannery and mining industries, etc., contains one or more toxic metal ions. Heavy metal ions as non-biodegradable compounds can be accumulated in living organisms easily and cause serious illnesses, such as cancer, damage to the nervous system, kidney failure and increasing blood and respiratory pressure. In addition, entry of toxic metal ions into food chain is possible through waste discharge into water bodies. Therefore, removing these metal ions from the wastewaters before discharging into environment is necessary (Rao *et al.*, 2007; García-Díaz *et al.*, 2018; Vuković *et al.*, 2010; Bystrzejewski and Pyrzyńska 2011; Tofighy and Mohammadi, 2011; Tofighy and Mohammadi, 2015).

Dyes as organic compounds with non-biodegradable and polluting nature are used in many industries including leather, paper, textile and plastic. About 750,000 tons of dye wastewaters are produced annually, worldwide. More than 10,000 dyes are available commercially which most of them have complex structures and are stable. Long-term exposure to dyes causes serious health problems including increased heart rate, shock, vomiting, eye burns, mental confusion, jaundice, cyanosis, limb paralysis, and tissue necrosis. Therefore, to reduce the dye impact on the organisms, dyes removal from wastewater before releasing into the environment is of great interest (Tan *et al.*, 2007, 2008; Choi *et al.*, 2018; Gherbia *et al.*, 2019; Sahu *et al.*, 2019; Etim, 2019; Tofighy and Mohammadi, 2014; Liu *et al.*, 2018; Franciski *et al.*, 2018; Lonappan *et al.*, 2016; Gong *et al.*, 2005).

Among the various methods of water/wastewater treatment including ion exchange, evaporation and condensation, chemical precipitation, electrodialysis, ultrafiltration, reverse osmosis, and adsorption, the last is one of the most promising methods from the view point of productivity, simplicity and economy (Tofighy and Mohammadi, 2011). Efficiency of the adsorption process depends on the adsorbent properties, directly (Tofighy and Mohammadi, 2015). Traditional adsorbents such as activated carbon (AC), coal, fly ash, zeolites, resins and etc. have limited practical applications due to their recovery problems and low adsorption capacity. Therefore, many efforts are being made to achieve new and high-yield adsorbents with high absorption capacity (Tofighy and Mohammadi, 2014). Recently, polymer matrix composites materials have shown significant potential as new adsorbents for water/wastewater treatment applications (Berber, 2020).

New materials are the basis of new technologies. In the twentieth century, with the advent of high-performance composites, as suitable alternative to traditional materials, much progress has been made in all scientific areas. Composite materials as a combination of two or more materials are composed of two main parts: matrix materials as continuous phase and filler materials as dispersed phase. The continuous phase can be metallic, ceramic or polymeric materials. The dispersed phase can be tubular, fiber, sheet and particle-like structure materials. The properties of composite materials directly depend on the properties of the continuous phase, the dispersed phase and their interfaces (Wang *et al.*, 2011).

Polymer matrix composite materials (PMCs) are defined as combination of inorganic or organic materials with polymers that provide new materials with new properties such as high mechanical strength and hardness, low density and optimal, chemical and thermal stability depending on the type of use. PMCs with high absorption capacity of dyes, heavy metal ions and other water pollutants can be used as effective adsorbents in water/wastewater treatment applications (Dongre *et al.*, 2019; Berber, 2020; Pandey *et al.*, 2017).

Carbon nanomaterials specially carbon nanotubes (CNTs) and graphene family including graphene oxide (GO) and reduced graphene oxide (rGO) with unique physical and chemical properties have received the researchers and scientist's attention worldwide and have encouraged them to use these nanomaterials to fabricate new PMCs for water/wastewater treatment applications.

In this article, current progresses in polymer matrix composites materials as adsorbent for water/wastewater treatment applications will be reviewed.

Bibliometric Analysis

The main aspects related to the applications of the polymer matrix composites materials in water/wastewater treatment can be identified by bibliometric analysis. Fig. 1 illustrates the number of scholarly studies including books, book articles, journal articles,

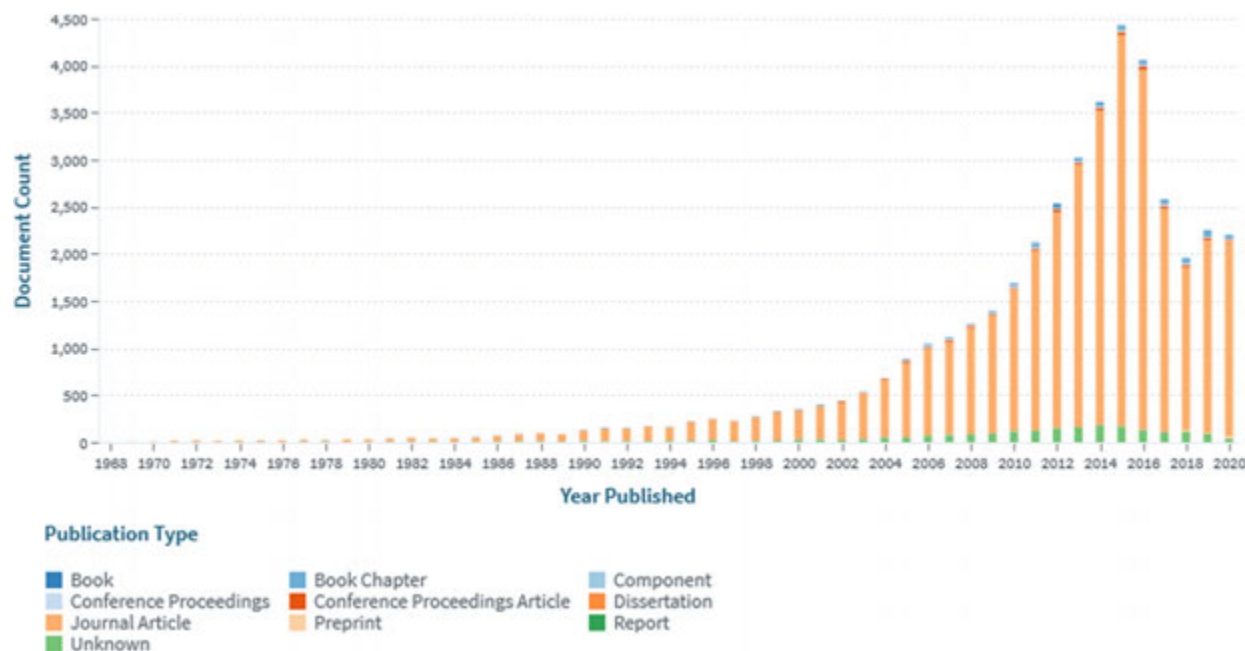


Fig. 1 Scholarly studies in the field of applications of the polymer matrix composites materials in water/wastewater treatment.

conference proceeding articles, dissertations, etc., in this research field, over time. As can be clearly observed, the number of scholarly studies accomplished over the years of 1980–2015 have been significantly increased and then over the years of 2015–2020 decreased to some extent. Among all of the scholarly works, the journal articles have the highest share 91.3%. **Fig. 2** shows the top publishers by the number of scholarly works in this field. As can be observed, the Elsevier publisher have been published the greatest number of the scholarly works in this research field.

Fig. 3 shows the clusters network visualization of the keywords with the most frequent co-occurrence in the field of the applications of the polymer matrix composites materials in water/wastewater treatment. This chart was obtained by importing the data downloaded from the Scopus into the VOSviewer software (version 1.6.15) and provided valuable information about the scholarly studies conducted so far in this research field. Each circle represents a keyword. The bigger the circle, the bigger the occurrence. The co-occurrence relationship between the keywords is presented by curves. Moreover, the distance between two keywords indicates the relationship strength, i.e., the closer the keywords, they are the more related and vice versa. As shown in **Fig. 3**, the keywords are divided into three clusters with different colors:

- (1) Cluster 1 (in green) mainly includes the keywords related to the topic of applications of polymer matrix composites as adsorbent, such as “adsorption”, “adsorbent”, “kinetic models”, “diffusion”, “isotherms”, “Langmuir”, “heavy metal”, “metal ions”, “kinetics”, “chitosan”, “water purification”, “pH”, “dye” and “removal efficiencies”.
- (2) Cluster 2 (in red) mainly includes the keywords related to the topic of applications of polymer matrix composites as membrane, such as “membranes”, “polymeric membranes”, “nanocomposite membranes”, “membrane fabrication”, “interfacial polymerization”, “thin film”, “desalination”, “osmosis”, “forward osmosis”, “thin film composite membrane”, “hydrophilicity”, “surface property”, “microfiltration” and “polyvinylidene fluoride”.
- (3) Cluster 3 (in blue) mainly includes the keywords related to the topic of polymer matrix composites fabrication and their properties, such as “optical properties”, “tensile strength”, “silica”, “carbon”, “graphene”, “catalyst activity”, “fillers”, “mesoporous”, “surface area”, “morphology”, “chemical composition”, “turbidity”, “solubility” and “polyvinyl alcohol”.

These three clusters reveal the major research directions in the field of applications of the polymer matrix composites materials in water/wastewater treatment. It is obvious that the polymer matrix composites materials can be used as adsorbent and membrane materials. Application of the polymer matrix composites materials as membrane materials has been reviewed frequently by other authors (Nasir *et al.*, 2019; Zahid *et al.*, 2018; Grylewicz and Mozia, 2020).

Adsorption

The “adsorption” word was first introduced by Heinrich Kayser, a German physicist, in 1881. The transfer of atoms, ions or molecules from the gas or liquid phase to the solid structure is called adsorption. The solid on which adsorption occurs is called “adsorbent” and the substance being adsorbed is called “adsorbate”. Adsorption capacity is defined as the amount of volume or mass of adsorbate per unit of adsorbent mass. The adsorption process can be done in both chemical and physical forms. The

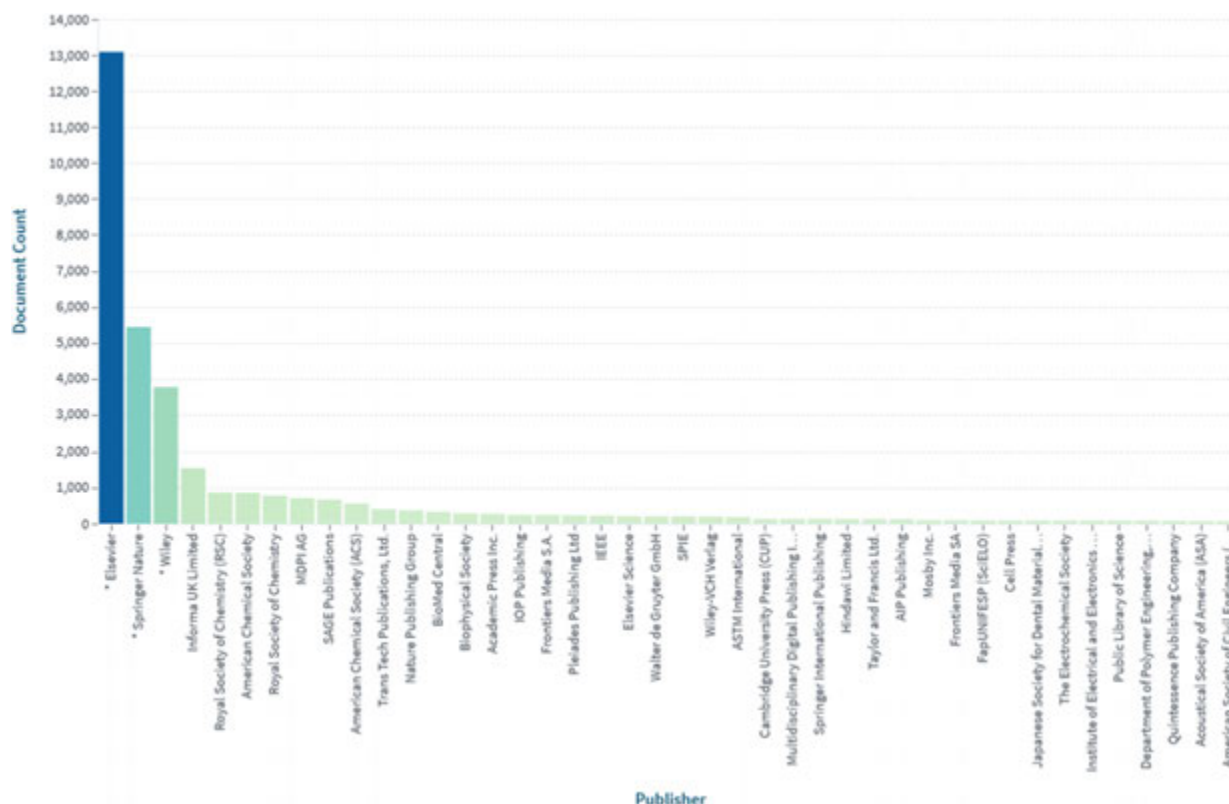
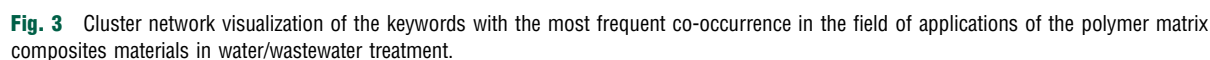


Fig. 2 The top publishers based on the number of accomplished scholarly studies in the field of applications of the polymer matrix composites materials in water/wastewater treatment. Reprinted from lens.org.

chemical adsorption (chemisorption) is done by chemical bonding (covalent bonding) between the adsorbent and the adsorbate. In physical adsorption (physisorption), the intermolecular forces between the adsorbate and the adsorbent are electrostatic or van der Waals interactions. Physical adsorption can be multilayer, but chemical adsorption is monolayer (Dąbrowski, 2001; Ruthven, 1984). The relationship between the equilibrium concentration of adsorbate (C_e) and the equilibrium adsorption capacity (q_e), at constant temperature, is described by adsorption isotherm models. There are numerous adsorption isotherm models including Langmuir, Freundlich, Redlich–Peterson, Sips and Liu isotherm models. Useful information about the adsorption mechanism, adsorbent/adsorbate interactions and surface properties can be achieved by the adsorption isotherm models parameters (Langmuir, 1918; Freundlich, 1906; Sips, 1948; Liu *et al.*, 2003; Redlich and Peterson, 1959; Tofighy and Mohammadi, 2010). Matching of the experimental data with the Langmuir and Freundlich isotherm models shows that adsorption is controlled by chemisorption (monolayer) and physisorption (multilayer), respectively. Also, valuable information about the adsorption process mechanism (physisorption or chemisorption) can be provided by adsorption kinetic studies by applying the adsorption kinetic models such as pseudo-first and second-order kinetic models and etc (Tofighy and Mohammadi, 2011; Lagergren, 1898; Blanchard *et al.*, 1984; Alencar *et al.*, 2012; Vaghetti *et al.*, 2009). Matching of the pseudo-first and pseudo-second order kinetic models with the experimental data shows that adsorption is controlled by physisorption and chemisorption, respectively (Senthilkumaar *et al.*, 2005; Oukil *et al.*, 2019; Tran *et al.*, 2016).

Composites

From the view point of materials science, human society has experienced the age of stone, bronze and iron. Composite materials as new materials were first introduced in the 1950s. Composite materials are composed of two or more components with different properties and different shapes. This combination not only preserves the properties of each component but also reveals new properties that are not available by any of the composite components (Petre *et al.*, 2015). Composite components are microscopically impermeable and have a distinct interface. Composites should have much better performance than each component. The development of composite materials as a multiphase system should be done using material design. Composite materials are composed of two main parts: matrix materials as continuous phase and filler materials as dispersed phase. The continuous phase can be made of metallic, ceramic or polymeric materials. Composites are classified based on the type of matrix materials including ceramic matrix composites (CMCs), metal matrix composites (MMCs) and polymer matrix composites (PMCs) as shown in Fig. 4. The dispersed phase can be tubular, fiber, sheet and particle-like structure materials including carbon nanomaterials, zeolites,



Polymer Matrix Composites (PMCs)

Polymer-organic composites adsorbents

Polyacrylonitrile (PAN) is considered as one of the most important precursors for polymer-organic composites fabrication. PAN-based PMCs are distinguished by their hardness, compatibility with polar substances and chemical stability and can be

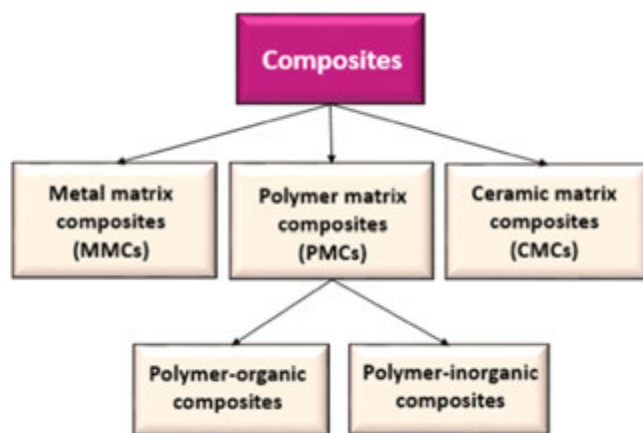


Fig. 4 Classification of composite materials.

functionalized easily to fabricate novel adsorbents for different applications including metal chelation and water/wastewater treatment (El-Aassar *et al.*, 2016). Poly(acrylonitrile-co-styrene), as an important copolymer of acrylonitrile and styrene, with superior properties including excellent chemical and heat resistance, high rigidity and superior transparency can be used as an effective adsorbent material for removal of harmful pollutants from wastewater (de Santa Maria *et al.*, 2001). Elkady *et al.* reported synthesis of a copolymer of acrylonitrile and styrene (poly(AN-co-ST)) via solution polymerization process. They fabricated nanofiber adsorbent using the synthesized poly(AN-co-ST) via electrospinning method, and to increase the dye adsorption capacity of the fabricated adsorbent, the nanofibers surface was functionalized by carboxylic acid groups via a simple chemical modification. It was found that after the nanofiber surface functionalization, the adsorption capacity of the basic violet dye reached 67.11 mg/g (in less than 30 min). Also, it was found that the both Langmuir and Temkin isotherm models well describe the dye adsorption behavior at equilibrium and the main decolorization rate controlling is the intraparticle diffusion kinetic model (Elkady *et al.*, 2016).

With combination of polymers and compounds containing different functional groups including carboxyl and amine, effective adsorbents can be fabricated for dyes removal from wastewater. PAN as a common and inexpensive commercial polymer with desirable thermal and chemical properties and good solubility in organic solvents is a desirable polymer for fabrication of composite nanofibers adsorbents via electrospinning technique for wastewater treatment applications (Deng *et al.*, 2003).

Almasian *et al.* incorporated diethylenetriamine (DETA) into PAN using electrospinning technique to fabricate DETA/PAN composite nanofibers with high dye adsorption capacity. Using alkali treatment, DETA was fixed to the polymer to hinder DETA releasing. It was found that DETA incorporation into PAN affects nanofibers morphology, directly. Also, it was found that the amount of adsorbed dye is influenced by the ratio of DETA added to the composite. Adsorption behavior of the fabricated DETA/PAN composite adsorbent matched well with the Langmuir isotherm model for C.I direct red 80 (DR80) dye removal (Almasian *et al.*, 2015).

Cyclodextrin-based composites with unique chemical and physical properties and porous structure have been extensively regarded by researchers for removing dyes from wastewater. The used of cyclodextrin as a practical adsorbent was limited due to its water solubility. To improve its insolubility, modification of cyclodextrin by self-crosslinking or immobilization through its abundant hydroxyl groups is an effective way (Liu *et al.*, 2020). Chen *et al.* reported fabrication of an eco-friendly composite adsorbent for removal of cationic dyes including crystal violet (CV), malachite green (MG), methylene blue (MB) and copper ion (Cu^{2+}) by crosslinking cyclodextrin polymer with polydopamine (CD-CA/PDA) that combines the advantages of both polydopamine and cyclodextrin. The fabrication steps of the CD-CA/PDA composite adsorbent are presented in Fig. 5. It was found that the fabricated CD-CA/PDA composite adsorbent with abundant carboxyl and catechol functional groups exhibits excellent adsorption properties. Also, it was found that the adsorption capacity of the fabricated CD-CA/PDA composite adsorbent is correlated to its functional groups and structural characteristics. The pseudo-second-order model matched well with the adsorption kinetic results demonstrating that adsorption is controlled by chemical adsorption. The fabricated CD-CA/PDA composite adsorbent exhibited great recyclability (at least 5 times) (Chen *et al.*, 2020).

Zhang *et al.* reported fabrication of β -Cyclodextrin (β -CD) immobilized with starch by introducing β -cyclodextrin as host functional molecule onto starch in presence of citric acid. The fabricated composite was used as a natural polymeric composite adsorbent for three cationic dyes (MB, basic fuchsin and methyl purple) removal from wastewater. It was found that the fabricated β -cyclodextrin-starch composite exhibits higher dye adsorption capacity than each of starch and β -cyclodextrin, separately that can be attributed to the functional groups of the starch- β -cyclodextrin composite including NH_2 , OH and COOH and the obtained irregular surface that plays significant role in the dye removal. It was found that the adsorption behavior of the fabricated composite adsorbent matches well with the both Langmuir and Freundlich isotherm models (Zhang *et al.*, 2019).

Cellulose is a biodegradable, linear and most abundant polysaccharide of β -D-glucopyranose units that are linked by β -1,4-glycosidic linkages. Vinyl monomers grafting on the hydroxyl (-OH) groups of cellulose is an effective way to enhance its physicochemical, hydrophilic/hydrophobic, swelling, thermal and mass-transfer properties (Kumar *et al.*, 2017; Hokkanen *et al.*, 2016).

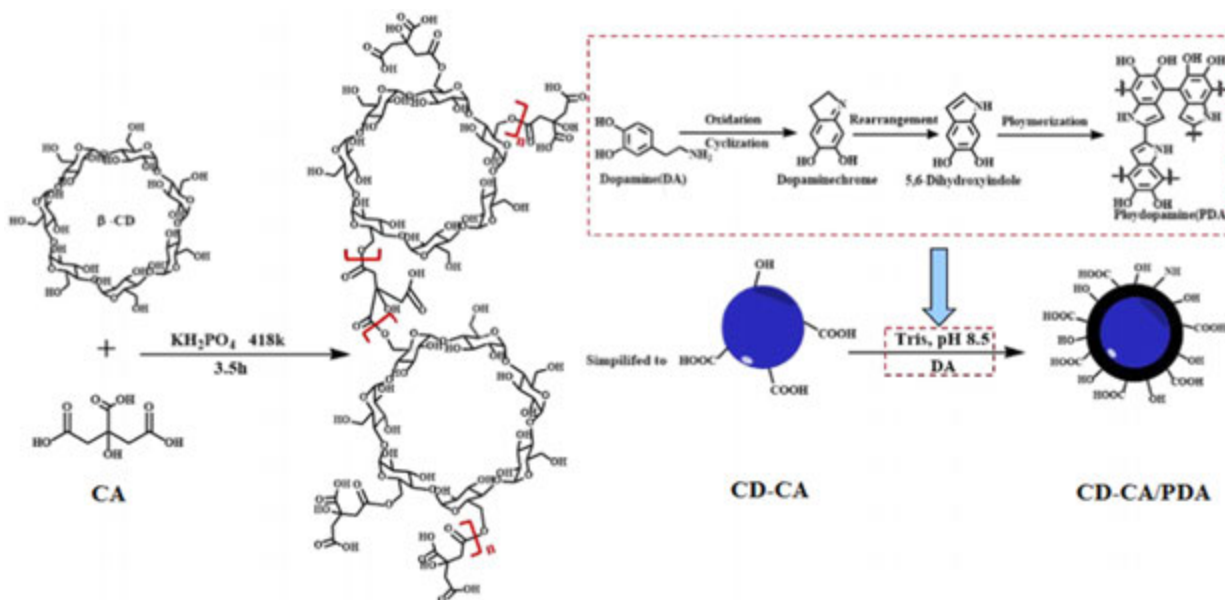


Fig. 5 The fabrication steps of the CD-CA/PDA composite adsorbent. Reproduced from Chen, H., Zhou, Y., Wang, J., Lu, J., Zhou, Y., 2020. Polydopamine modified cyclodextrin polymer as efficient adsorbent for removing cationic dyes and Cu_2 . *Journal of Hazardous Materials* 389, 121897.

Yue *et al.* reported fabrication of an efficient composite adsorbent for dyes removal from wastewater by grafting beta-cyclodextrin (β -CD) and amino-terminated hyperbranched polymer (NH_2 -HBP) onto cotton fibers as a kind of renewable, eco-friendly and abundant cellulose fiber in nature. The fabricated composite adsorbent exhibited remarkable adsorption properties for dyes (Congo red (CR) and MB) removal that can be related to its functional groups. It was found that pH value has great effect on the adsorption capacity of dyes (Yue *et al.*, 2017).

Kumar *et al.* reported fabrication of a highly efficient co-polymer composite adsorbent for dye removal from wastewater by functionalization of cellulose extracted from agricultural wastes through free radical grafting with a binary vinyl monomer mixture of acrylic acid and 2-acrylamido – 2- methylpropane sulfonic acid in the presence of cross-linker ($\text{N,N}'$ -methylene bisacrylamide). The adsorption behavior of the fabricated copolymer (Cell-g-AASO3H-co-AAc) was studied for removal of MG, CV, CR dyes and Cu(II) and Ni(II) metal ions from aqueous solutions. It was found that the experimental adsorption data are well fitted with the pseudo-second-order kinetic model and the Langmuir isotherm model. SEM images of the neat cellulose and the fabricated Cell-g-AASO3H-co-AAc composite adsorbents are shown in Fig. 6. (Kumar *et al.*, 2018).

Zhu *et al.* reported functionalization of cellulose with hyper-branched polyethylenimine (HPEI) as an amino-rich cationic polyelectrolyte to fabricate HPEI-CE polymer composite adsorbent for anionic (CR) and cationic (BY28) dyes removal from aqueous solution. The aldehyde groups on the surface of chemically oxidized cellulose are covalently linked with NH_2 groups of HPEI. It was found that the adsorption behavior of the fabricated HPEI-CE composite adsorbent matches well with the Langmuir isotherm model with maximum adsorption capacity of 1860 mg/g for BY28 and 2100 mg/g for CR, respectively. It was found that the hyper-branched structure of the polymer composite adsorbent improves the interparticle dye molecules diffusion into the composite (Zhu *et al.*, 2016).

In order to rise the adsorption capacity of polymers, copolymerization process can be performed in which a new polymer with improved properties is obtained by combining one or more polymers with each other (Abdullah *et al.*, 2019).

Hosseinzadeh *et al.* reported fabrication of a composite adsorbent by modification of poly(styrene-maleicanhydride) copolymer (SMA) with 3-(4-hydroxy phenyl) cyclopropane-1,1,2,2-tetramethyleneamine (HPCA) and subsequently reacting the product (SMA-HPCA) with 1,2-diaminoethane (DAE) for preparation of tridimensional chelating resin (CSMA-HPCA) as a new copolymer with multiprimary amines cyclopropane functionalities in the pendant group for heavy metal ions (Cu(II) , Pb(II) , Zn(II)) removal from aqueous solution. It was found that the adsorption behavior of the synthesized CSMA-HPCA composite adsorbent follows the pseudo-second order kinetic and the Langmuir isotherm models (Hosseinzadeh, 2018).

Chen *et al.* reported fabrication of a novel polyamine-type starch/glycidyl methacrylate copolymer by copolymerization of corn starch and glycidyl methacrylate (GMA) and a subsequent amination reaction between epoxy groups of GMA and amino groups (NH_2) of diethylenetriamine. The fabricated composite adsorbent was used for heavy metal ions (Pb(II) , Cu(II) , Cr(III) and Cd(II)) removal from wastewater. The maximum adsorption capacities of the fabricated composite adsorbent for Cu(II) , Pb(II) , Cd(II) and Cr(III) were achieved up to 2.33, 1.25, 0.83 and 0.56 mmol g^{-1} , respectively. The fabricated adsorbent exhibited high adsorption capacity and excellent reusability (high adsorption capacity after 10 cycles of adsorption/desorption tests) (Chen *et al.*, 2018).

Yu *et al.* covalently linked EDTA-modified chitosan (CS-EDTA), β -cyclodextrin (β -CD) and pentafluoropyridine together to fabricate porous organic polymeric composite adsorbents for efficient heavy metal ions (Ni(II) , Pb(II) , Hg(II) , Co(II) , Cu(II) , Cr(II)) removal from wastewater. The fabricated composite adsorbents exhibited high adsorption capacity and good reusability (high adsorption capacity after 5 cycles of adsorption-desorption experiments) (Yu *et al.*, 2018).

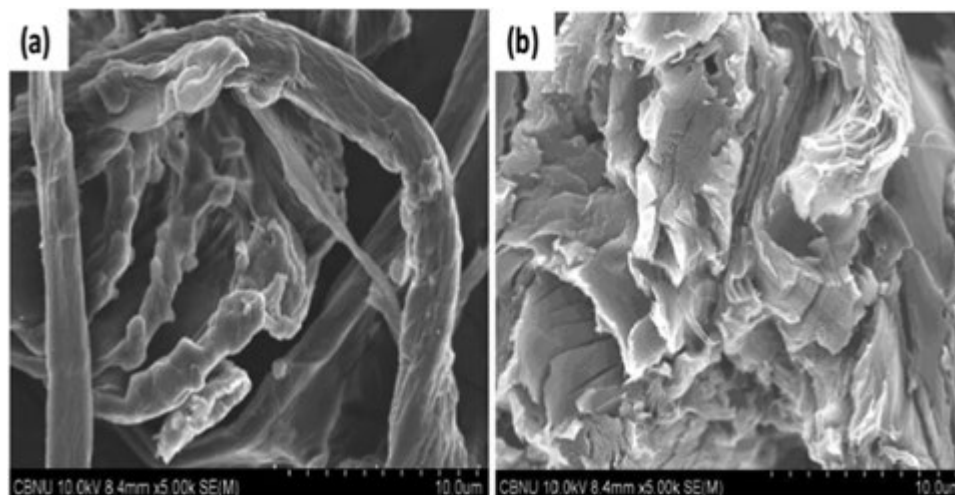


Fig. 6 SEM images of the neat cellulose and the fabricated Cell-g-AAS03H-co-AAC composite adsorbents. Reproduced from Kumar, R., Sharma, R.K., Singh, A.P., 2018. Removal of organic dyes and metal ions by cross-linked graft copolymers of cellulose obtained from the agricultural residue. *Journal of Environmental Chemical Engineering* 6, 6037–6048.

Among the polymer-based adsorbents, conducting polymer-based adsorbents like polyethylenimine (PEI), polypyrrole (Ppy), polyaniline (PANI) and their composites have received great attention as appropriate adsorbents for various heavy metal ions removal due to their low cost, ease of synthesis and regeneration and high chemical and mechanical stability (Mahmud *et al.*, 2006). Also, their highly porous structure and ion exchange capacities have also attracted researchers. The conducting polymer-based composites can be used effectively for different heavy metal ions removal from wastewater (Mahmud *et al.*, 2016). Polypyrrole as a conducting polymer containing positively charged nitrogen atoms with appropriate properties can be used to fabricate the polypyrrole based composites for heavy metal ions removal due to its biocompatibility properties and simple fabrication process. (Mahmud *et al.*, 2016; Yao *et al.*, 2009) Mahmud *et al.* published a review paper about heavy metal ions removal from water/wastewater by the polypyrrole-based composite adsorbents (Mahmud *et al.*, 2016).

Understanding the interactions between functional groups of polymer composites with various pollutants is very important because it will conduct the future studies to achieve the optimum removal efficiency of the target contaminants.

Polymer-inorganic composite adsorbents

Among a wide variety of known inorganic nanomaterials, carbon nanomaterials have recently attracted tremendous attention. Among carbon nanomaterials, carbon nanotubes (CNTs) and graphene oxide (GO) with unique properties could improve adsorption capacity of the polymer matrix composites, significantly.

CNTs-based PMCs

CNTs as an important member of the carbon nanomaterials family, have unique properties such as high specific surface area, low mass density, high thermal stability and mechanical stiffness, frictionless surface, high flexibility, ability to form π - π interactions with aromatic compounds, and high aspect ratio (length to diameter ratio more than 1000) and can be easily surface modified. Among the several nanomaterials based adsorbents, CNTs with greater available specific surface area, hollow structure, hydrophobic nature, higher porosity, ease of functionalization and well-developed micro and meso-pores have been recognized as excellent adsorbent for removal of various pollutants. CNTs as cylindrical macromolecules composed of sp^2 hybridized carbon atoms are divided into three categories of single-walled (SWCNTs), double-walled (DWCNTs) and multi-walled carbon nanotubes (MWCNTs) as shown in Fig. 7 (Tofighy and Mohammadi, 2011; Tofighy and Mohammadi, 2019; Mashkooor and Nasar, 2020; Tofighy and Mohammadi, 2020; Tofighy and Mohammadi, 2012).

Chemical or physical functionalization of CNTs with polymers is regarded as one of the most effective methods to increase hydrophilicity and water solubility as well as CNTs adsorption properties. The CNTs-based composites have received increasing attention for adsorptive removal of contaminants from wastewater. The CNTs-based composites with enhanced adsorption capability can be fabricated via surface functionalization of CNTs with polymers as an effective approach.

Bankole *et al.* functionalized CNTs with polyhydroxybutyrate to fabricate efficient composite adsorbent (PHB-CNTs) for heavy metal ions (As, Pb, Cr, Cd, Ni, Cu, Fe, and Zn) removal from wastewater. It was found that hydrophilic characteristics and adsorption capacities of CNTs are enhanced after functionalization with the polymer, significantly. It was found that the adsorption behavior of the synthesized adsorbent fits well with the Temkin isotherm and the pseudo-second-order kinetic models (Bankole *et al.*, 2019).

Dendrimers with abundant surface functional groups including carboxyl, amine and hydroxyl can lead to enhance the heavy metal ions adsorption capacity of CNTs. Hayati *et al.* coated CNTs with polyamidoamine dendrimer (PAMAM) and the fabricated

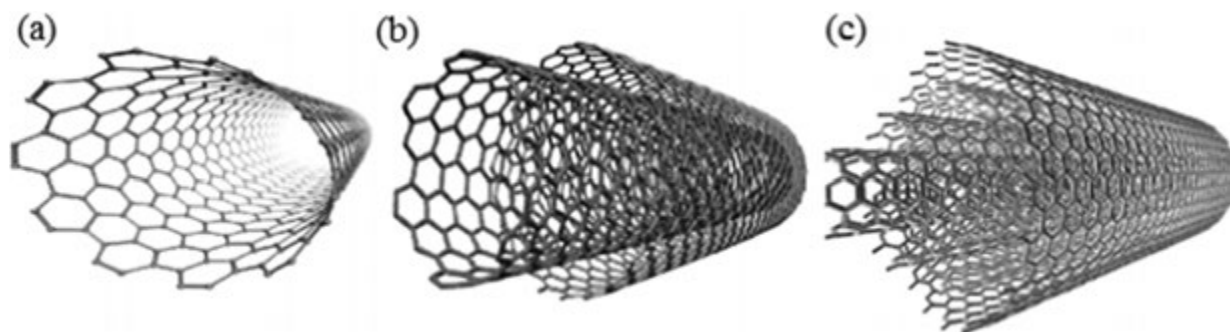


Fig. 7 Scheme of (a) SWCNT, (b) DWCNT and (c) MWCNT.

composite was used as adsorbent for heavy metal ions removal. The fabricated composite exhibited significant adsorption capacities of As(III), Co(II), and Zn(II) ions as 432, 494, and 470 mg/g, respectively. A schematic of the fabrication process for the PAMAM-CNTs composite adsorbent is shown in [Fig. 8](#) ([Hayati et al., 2018](#)).

Hydrogels can be widely used as effective adsorbent in water treatment application due to their low cost, facile preparation and high adsorption capacity. Yue *et al.* reported fabrication of polyacrylamide (PAAm)-sodium alginate (SA) interpenetrating polymer network-structured hydrogels through in situ polymerization method. Then, they incorporated CNTs into the PAAm-SA matrix via hydrogen bonding. The fabricated hydrogel with macroporous structure exhibited high water content ($\approx 83\%$) and low density ($\approx 1.4 \text{ g/cm}^3$). It was found that CNTs addition improves elasticity, mechanical strength and adsorption capacity of the fabricated hydrogel. Also, it was found that compared to the neat hydrogel, adsorption capacity of the fabricated CNTs-based hydrogel increases 1.28 times ([Yue et al., 2019](#)).

Kumar *et al.* reported fabrication of MWCNTs-polyaniline (Pani) composite via oxidation polymerization methodology. Then, the fabricated composite was doped with hydrophilic groups of para-toluene-sulfonic acid. These additional functional groups enhanced water dispersion and adsorption capacity of the prepared composite. The as-synthesized pTSA-Pani@CNT composite was used as adsorbent for hexavalent chromium (Cr(VI)) removal from aqueous solution. It was found that the as-synthesized pTSA-Pani@CNT composite exhibits higher Cr(VI) adsorption capacity than the pTSA-CNT and pTSA-Pani composites. A schematic illustration representing fabrication of the pTSA-Pani@CNT composite adsorbent for adsorptive removal of Cr(VI) is shown in [Fig. 9](#) ([Kumar et al., 2019](#)).

Xie *et al.* reported fabrication of poly (sodium-p-styrene sulfonate) modified CNTs (PDA-PSPSH-CNT) composite adsorbent for cationic dye (MB) removal from aqueous solution. It was found that the adsorption capacity of MB is inversely proportional to temperature and directly proportional to contact time. It was found that the fabricated PDA-PSPSH-CNT composite adsorbent with the maximum adsorption capacity of MB as 160 mg/g, exhibits excellent adsorptive property ([Xie et al., 2015](#)).

Wu *et al.* reported fabrication of O-MWCNTs/PANI composite adsorbent based on MWCNTs encapsulation by polyaniline (PANI) via in situ polymerization method for adsorptive removal of alizarin yellow dye from wastewater (with maximum adsorption capacity of 884.80 mg/g). It was found that the adsorption behavior of the fabricated O-MWCNTs/PANI composite adsorbent fits well by the Langmuir isotherm and the pseudo-second-order kinetic models. Also, it was found that the fabricated O-MWCNTs/PANI composite adsorbent exhibits higher adsorption capacity than the pristine PANI or MWCNTs ([Wu et al., 2018](#)).

Mallakpour *et al.* recycled poly(ethylene terephthalate) (PET) bottle waste and fabricated PET/carboxyl-functionalized MWCNTs for adsorptive removal of Cd (II) metal ions from aqueous solution. It was found that the fabricated composite exhibits high adsorption capacity of Cd (II) metal ions, high electrical conductivity as well as good flame retardancy ([Mallakpour and Behranvand, 2017](#)).

Zarghami *et al.* reported fabrication of polyvinyl alcohol/chitosan composite adsorbent containing acid-functionalized CNTs (PVA/CS-CNTs) via solution casting method for adsorption of lead and zinc metal ions from aqueous solutions. It was found out that the adsorption behaviors of zinc and lead metal ions using the fabricated CS/PVA-CNTs composite adsorbent match well with the pseudo-first-order kinetic model and the Freundlich isotherm model ([Zarghami et al., 2015](#)).

GO-based PMCs

Graphene as a two-dimensional monolayer of sp^2 -hybridized carbon atoms is the basic building block of all other graphitic carbon allotropes. GO as an important member of graphene family with many attractive properties such as hydrophilic nature, superior mechanical stability, good miscibility with polymers, high flexibility and its negatively charged surface can be incorporated into polymer matrices to fabricate composite adsorbent. GO as a well-known inorganic nanomaterial with abundant oxygen-containing functional groups on its basal plane and edges (hydroxyl (-OH) and epoxy (C-O-C) groups in the basal plane and carboxylic acid (-COOH) groups at the edges) displays an extensive prospect in water and wastewater treatment field. These functional group can provide high density of negatively charge as suitable sites for removal of adsorbates with positively charge including heavy metal ions ([Mishra and Ramaprabhu, 2011](#); [Ren et al., 2013](#)) and cationic dyes ([Ramesha et al., 2011](#); [Yang et al., 2011](#)). Also, existence of the oxygen-containing functional groups on the GO structure facilitates chemical modification of GO to enhance its adsorption capacity.

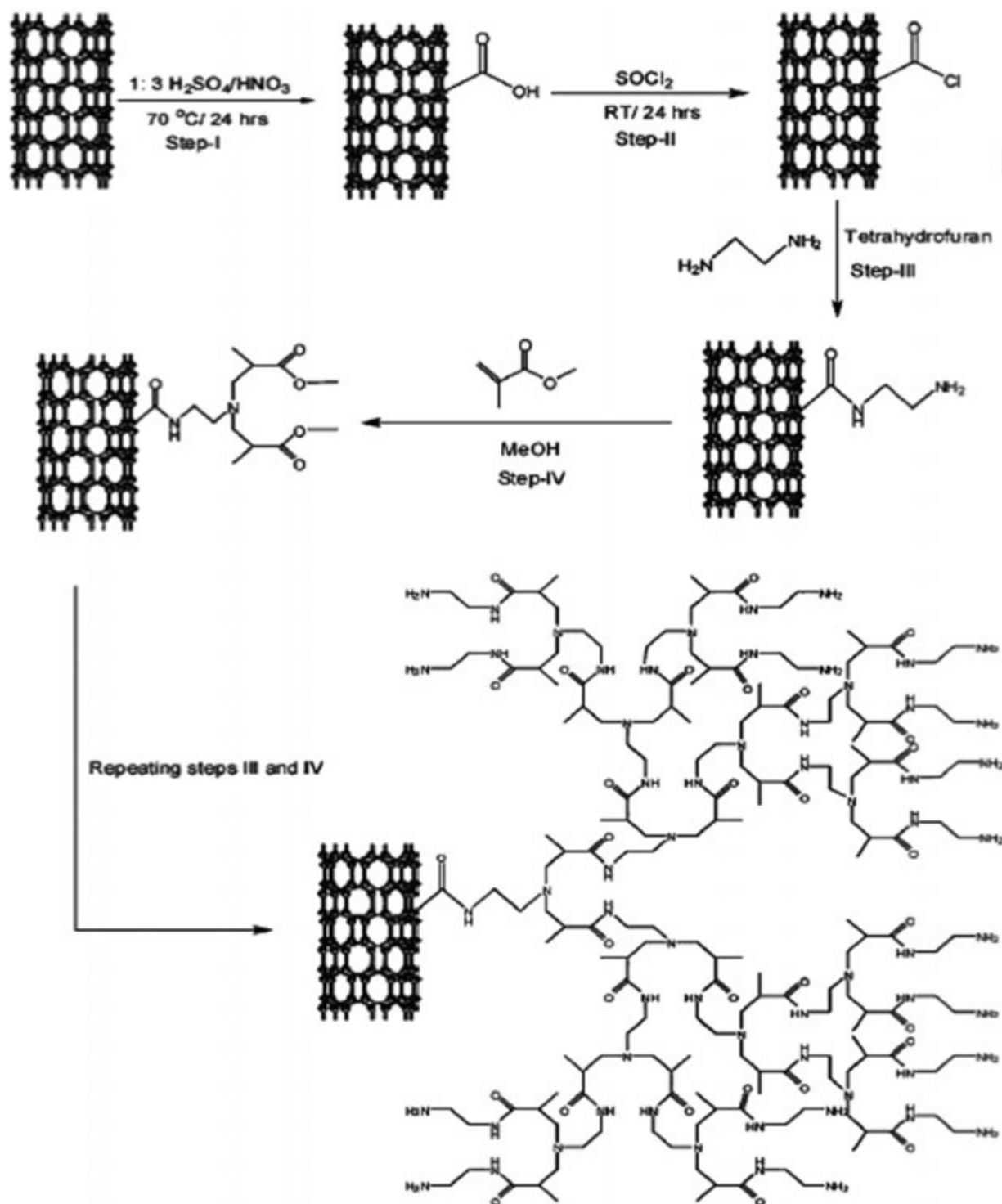


Fig. 8 A schematic of the PAMAM-CNTs composite adsorbent fabrication process. Reproduced from Hayati, B., Maleki, A., Najafi, F., *et al.*, 2018. Heavy metal adsorption using PAMAM/CNT nanocomposite from aqueous solution in batch and continuous fixed bed systems. *Chemical Engineering Journal* 346, 258–270.

Beside GO, reduced GO (rGO) can also be used as adsorbent for environmental applications (Ramesha *et al.*, 2011; Tiwari *et al.*, 2013; Pan *et al.*, 2013). The rGO can be prepared through chemical or thermal reduction of GO to decrease its oxygen content (partial deoxygenation) (Bianco *et al.*, 2013). A schematic illustration of graphene, GO and rGO is shown in Fig. 10.

Chandra *et al.* reported fabrication of polypyrrole–reduced graphene oxide (PPy-rGO) composite adsorbent via a chemical route for adsorptive removal of Hg(II) from aqueous solution. It was observed that the pyrrole polymerized along graphene

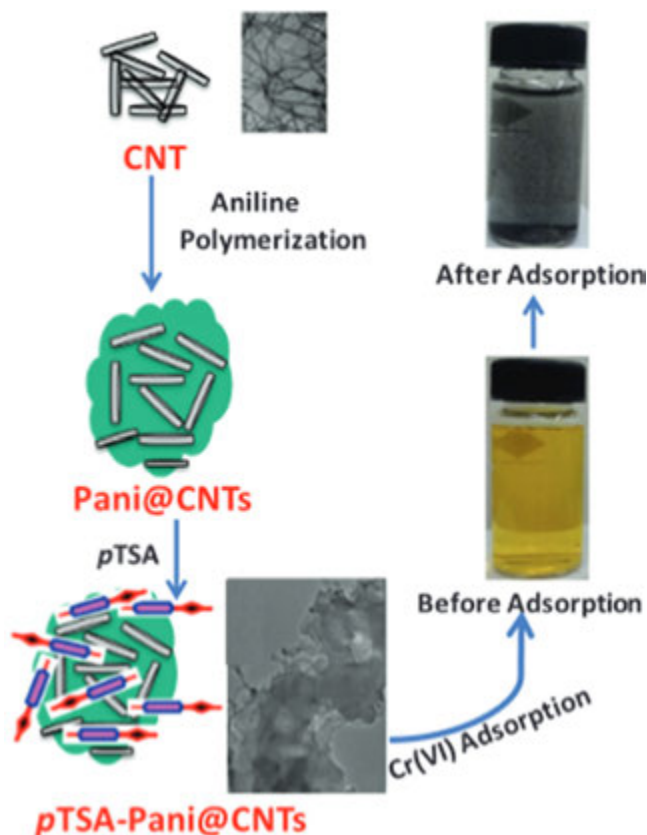


Fig. 9 A schematic illustration of the pTSA-Pani@CNT composite adsorbent fabrication for adsorptive removal of Cr(VI). Reproduced from Kumar, R., Ansari, M.O., Alshahrie, A., *et al.*, 2019. Adsorption modeling and mechanistic insight of hazardous chromium on para toluene sulfonic acid immobilized-polyaniline@ CNTs nanocomposites. *Journal of Saudi Chemical Society* 23, 188–197.

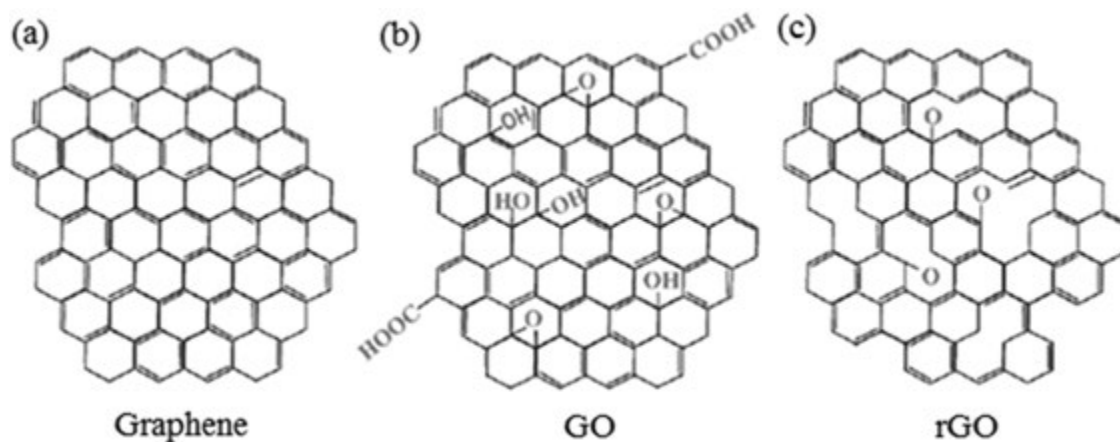


Fig. 10 Schemes of (a) Graphene, (b) GO and (c) rGO.

nanosheets exhibits an enhanced surface area. The fabricated PPy-rGO composite as a stable and environmentally friendly adsorbent exhibits excellent adsorption capacity for Hg(II) as high as 980 mg/g (Chandra and Kim, 2011).

Li *et al.* reported fabrication of polyaniline-reduced graphene oxide (PANI-rGO) composite adsorbent through aniline polymerization in the presence of GO and reduction by hydrazine hydrate for adsorptive removal of Hg(II) from aqueous solution. As reported, compared to PANI, the maximum adsorption capacity of the fabricated PANI-rGO composite adsorbent for Hg(II) is enhanced from 515 to 1000 mg/g that is due to the presence of rGO resulting in 7 times enhancement in adsorption sites and specific surface area. Also, nitrogen-containing functional groups in polyaniline structure act as adsorption sites for heavy metal ions removal (Li *et al.*, 2013).

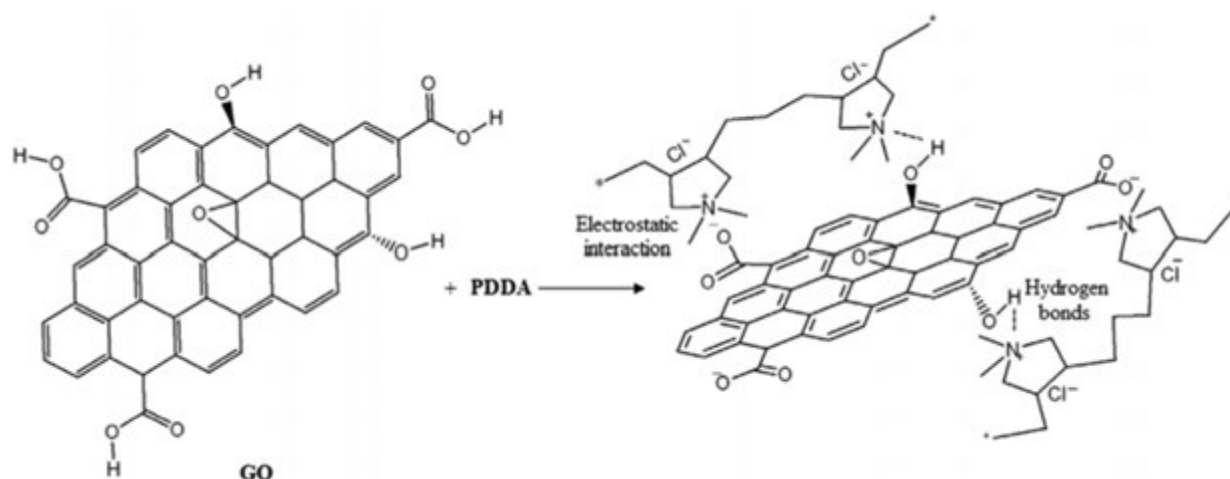


Fig. 11 A schematic illustration for fabrication procedure of the PDDA/GO composite adsorbent. Reproduced from Wang, X., Liu, Z., Ye, X., *et al.*, 2014. A facile one-step approach to functionalized graphene oxide-based hydrogels used as effective adsorbents toward anionic dyes. *Applied Surface Science* 308, 82–90.

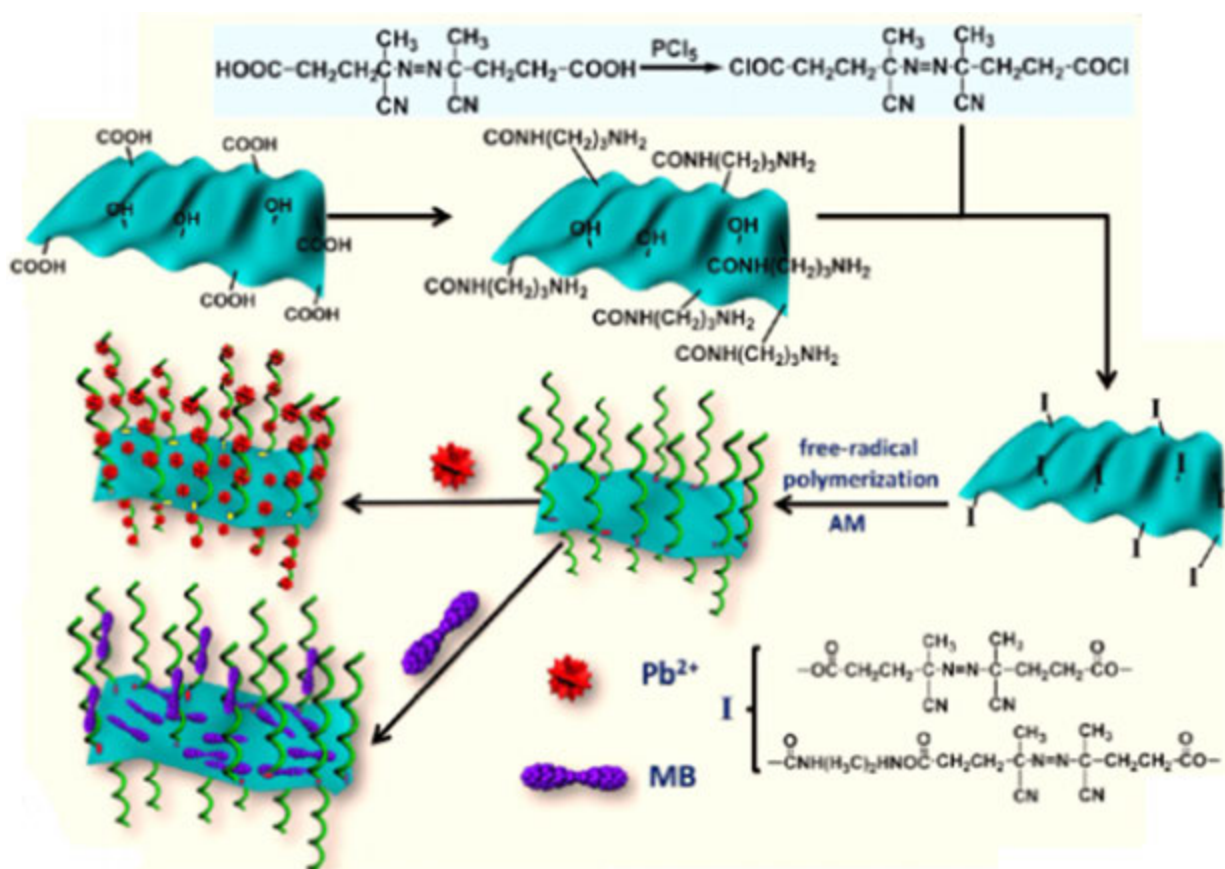


Fig. 12 A synthesis illustration for fabrication procedure of the PAM/rGO composite adsorbent. Reproduced from Yang, Y., Xie, Y., Pang, L., *et al.*, 2013. Preparation of reduced graphene oxide/poly (acrylamide) nanocomposite and its adsorption of Pb (II) and methylene blue. *Langmuir* 29, 10727–10736.

Fan *et al.* reported fabrication of graphene oxide-sodium alginate-polyacrylamide (GO-SA-PAM) composite hydrogel adsorbent with excellent mechanical property through free-radical polymerization of SA and acrylamide (AAM) in the presence of GO in an aqueous system followed by crosslinking with Ca^{2+} . GO nanosheets were used as reinforcing filler and due to hydrogen bonding between the O–H bond of GO nanosheets and the N–H bond of PAM, mechanical properties of the fabricated composite improved, significantly. It was

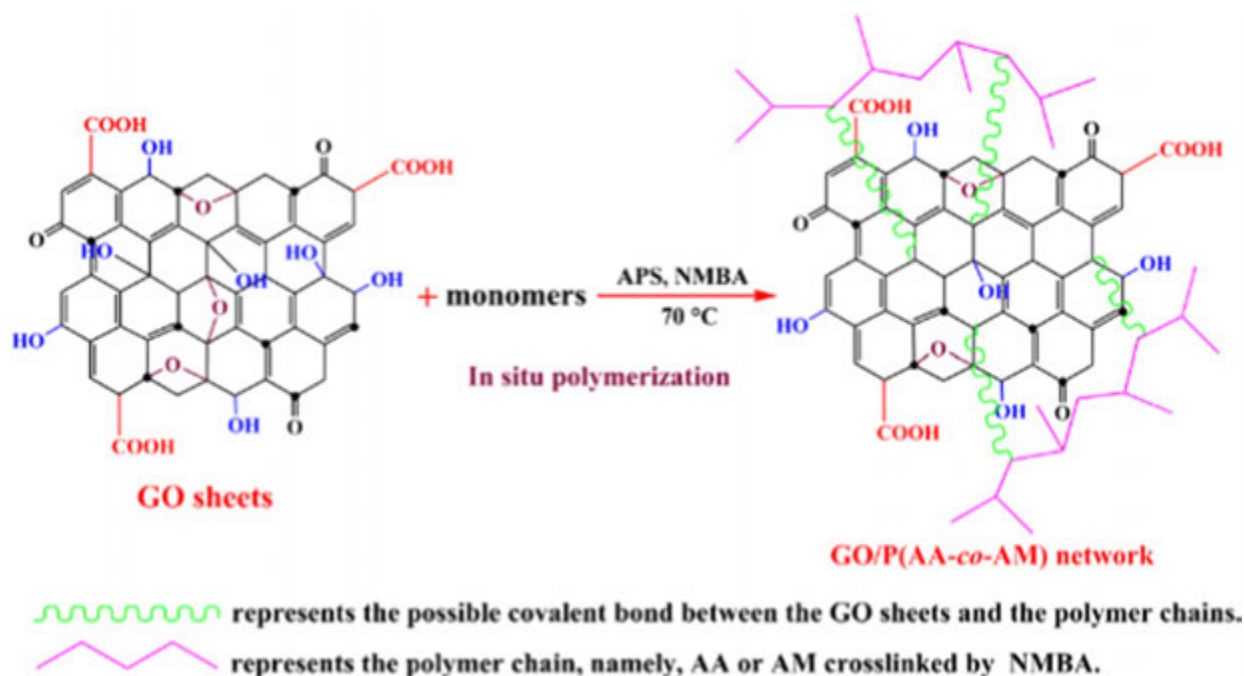


Fig. 13 A schematic illustration for fabrication procedure of the GO/P(AA-co-AM) composite absorbent. Reproduced from Huang, Y., Zeng, M., Ren, J., *et al.*, 2012. Preparation and swelling properties of graphene oxide/poly (acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 401, 97–106.

found that the fabricated GO-SA-PAM composite adsorbent exhibits high adsorption capacities for numerous anionic and cationic dyes. Also, after the GO incorporation into the composite adsorbent, the dyes adsorption capacities improve, significantly (Fan *et al.*, 2013).

Wang *et al.* reported fabrication of poly(diallyldimethylammonium chloride)-graphene oxide (PDDA-GO) hydrogel composite adsorbent through self-assembling method for adsorption of anionic dyes from aqueous solution. It was found that the fabricated PDDA/GO composite adsorbent exhibits high removal efficiency for both trypan blue (TB) and ponceau S (PS) anionic dyes due to the strong anion-cation and π - π interactions. Also, the adsorption behavior of the fabricated PDDA/GO composite adsorbent fits well with the pseudo-second-order kinetic model. A schematic illustration for fabrication procedure of the PDDA/GO composite adsorbent is shown in Fig. 11 (Wang *et al.*, 2014).

Yang *et al.* reported fabrication of poly(acrylamide)/rGO composite adsorbent (PAM/rGO) by synthesis of poly(acrylamide) polymer brushes on the rGO nanosheets through in situ free-radical polymerization for adsorptive removal of Pb(II) metal ions and MB from aqueous solutions. It was found that the adsorption behavior of the fabricated PAM/rGO composite adsorbent well fits with the Langmuir isotherm model and the pseudo-second-order model. The fabricated PAM/rGO composite adsorbent exhibits adsorption capacities as high as 1530 and 1000 mg/g for MB and Pb(II), respectively. A schematic illustration for fabrication procedure of the PAM/rGO composite adsorbent is shown in Fig. 12 (Yang *et al.*, 2013).

Huang *et al.* reported fabrication of GO/poly(acrylic acid-co-acrylamide) composite absorbent through in situ radical polymerization. It was found that owing to the possible hydrogen and covalent bonds between polymer chains and GO, GO can be dispersed well in the polymer matrix and this increases the intermolecular interactions between the components, effectively. A schematic illustration for fabrication procedure of the GO/P(AA-co-AM) composite absorbent is shown in Fig. 13 (Huang *et al.*, 2012).

Cheng *et al.* reported fabrication of GO/poly(acrylic acid) composite adsorbent (GO/PAA) for adsorptive removal of MB from aqueous solution. It was found that the fabricated PAA/GO composite has an interconnected three-dimensional porous network, which enhances its adsorption capacity by allowing the adsorbate (MB) molecules to diffuse easily into its porous structure. The highest MB adsorption capacity of the prepared PAA/GO composite adsorbent reaches as high as 1600 mg/g. It was found that the adsorption behavior of the prepared PAA/GO composite adsorbent matches well with the Langmuir isotherm model and the pseudo-second-order kinetic model and the adsorption process is controlled by the intraparticle diffusion model (Cheng *et al.*, 2014).

Conclusions

Polymer matrix composites (PMCs) as a combination of polymers with other organic or inorganic materials with high adsorption capacity of heavy metal ions, dyes and other water pollutants can be used in water/wastewater treatment applications as adsorbent, effectively. Carbon nanomaterials as inorganic nanofillers with unique chemical and physical properties can improve the PMCs performance in terms of adsorption capacity and mechanical, chemical and thermal resistance. Although the carbon nanomaterials

based-PMCs adsorbents are promising in laboratory studies, in order to commercialize the carbon nanomaterials-PMCs adsorbents for practical applications in very near future, a lot of research work should be performed. The future commercialization and development of the carbon nanomaterials based-PMCs adsorbents face a variety of challenges including potential environmental and human risk, cost-effectiveness and technical hurdles. Therefore, prior to the application of the carbon nanomaterials specially CNTs in water/wastewater treatment, deep toxic studies are crucially needed. Also, further efforts to decrease the carbon nanomaterials cost make brighter future for the carbon nanomaterials based-PMCs adsorbents in the water/wastewater treatment sector.

References

- Abdullah, N., Yusof, N., Lau, W., Jaafar, J., Ismail, A., 2019. Recent trends of heavy metal removal from water/wastewater by membrane technologies. *Journal of Industrial and Engineering Chemistry* 76, 17–38.
- Alencar, W.S., Lima, E.C., Royer, B., *et al.*, 2012. Application of acai stalks as biosorbents for the removal of the dye Procion Blue MX-R from aqueous solution. *Separation Science and Technology* 47, 513–526.
- Almasian, A., Olya, M.E., Mahmoodi, N.M., 2015. Preparation and adsorption behavior of diethylenetriamine/polyacrylonitrile composite nanofibers for a direct dye removal. *Fibers and Polymers* 16, 1925–1934.
- Bankole, M.T., Abdulkareem, A.S., Mohammed, I.A., *et al.*, 2019. Selected heavy metals removal from electroplating wastewater by purified and polyhydroxybutyrate functionalized carbon nanotubes adsorbents. *Scientific Reports* 9, 1–19.
- Berber, M.R., 2020. Current advances of polymer composites for water treatment and desalination. *Journal of Chemistry* 2020.
- Bianco, A., Cheng, H.-M., Enoki, T., *et al.*, 2013. All in the graphene family – A recommended nomenclature for two-dimensional carbon materials. *Carbon* 65, 1–6.
- Blanchard, G., Maunay, M., Martin, G., 1984. Removal of heavy metals from waters by means of natural zeolites. *Water Research* 18, 1501–1507.
- Bystrzejewski, M., Pyrzyńska, K., 2011. Kinetics of copper ions sorption onto activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 377, 402–408.
- Chandra, V., Kim, K.S., 2011. Highly selective adsorption of Hg^{2+} by a polypyrrole-reduced graphene oxide composite. *Chemical Communications* 47, 3942–3944.
- Chen, H., Zhou, Y., Wang, J., Lu, J., Zhou, Y., 2020. Polydopamine modified cyclodextrin polymer as efficient adsorbent for removing cationic dyes and Cu_2 . *Journal of Hazardous Materials* 389, 121897.
- Chen, Y., Zhao, W., Wang, H., Meng, X., Zhang, L., 2018. A novel polyamine-type starch/glycidyl methacrylate copolymer for adsorption of Pb (II), Cu (II), Cd (II) and Cr (III) ions from aqueous solutions. *Royal Society Open Science* 5, 180281.
- Cheng, C., Liu, Z., Li, X., *et al.*, 2014. Graphene oxide interpenetrated polymeric composite hydrogels as highly effective adsorbents for water treatment. *RSC Advances* 4, 42346–42357.
- Choi, H.-J., Yu, S.-W., Choi, H.-J., Yu, S.-W., 2018. Biosorption of methylene blue from aqueous solution by agricultural bioadsorbent corncob. *Environmental Engineering Research* 24, 99–106.
- Dąbrowski, A., 2001. Adsorption – From theory to practice. *Advances in Colloid and Interface Science* 93, 135–224.
- de Santa Maria, L.C., Amorim, M.C., Aguiar, M.R., *et al.*, 2001. Chemical modification of cross-linked resin based on acrylonitrile for anchoring metal ions. *Reactive and Functional Polymers* 49, 133–143.
- Deng, S., Bai, R., Chen, J., 2003. Behaviors and mechanisms of copper adsorption on hydrolyzed polyacrylonitrile fibers. *Journal of Colloid and Interface Science* 260, 265–272.
- Dongre, R.S., Sadasivuni, K.K., Deshmukh, K., *et al.*, 2019. Natural polymer based composite membranes for water purification: A review. *Polymer-Plastics Technology and Materials* 58, 1295–1310.
- El-Aassar, M., El-Kady, M., Hassan, H.S., Al-Deyab, S.S., 2016. Synthesis and characterization of surface modified electrospun poly (acrylonitrile-co-styrene) nanofibers for dye decolorization. *Journal of the Taiwan Institute of Chemical Engineers* 58, 274–282.
- Elkady, M.F., El-Aassar, M.R., Hassan, H.S., 2016. Adsorption profile of basic dye onto novel fabricated carboxylated functionalized co-polymer nanofibers. *Polymers* 8, 177.
- Etim, E.U., 2019. Removal of methyl blue dye from aqueous solution by adsorption onto ground nut waste. *Biomedical Journal of Scientific & Technical Research* 15, 11365–11371.
- Fan, J., Shi, Z., Lian, M., Li, H., Yin, J., 2013. Mechanically strong graphene oxide/sodium alginate/polyacrylamide nanocomposite hydrogel with improved dye adsorption capacity. *Journal of Materials Chemistry A* 1, 7433–7443.
- Franciski, M.A., Peres, E.C., Godinho, M., *et al.*, 2018. Development of CO_2 activated biochar from solid wastes of a beer industry and its application for methylene blue adsorption. *Waste Management* 78, 630–638.
- Freundlich, H., 1906. Adsorption in solution. *Journal of Physical Chemistry*. 1361–1368.
- García-Díaz, I., López, F.A., Alguacil, F.J., 2018. Carbon nanofibers: A new adsorbent for copper removal from wastewater. *Metals* 8, 914.
- Gherbia, A., Chergui, A., Yeddou, A., Ammar, S.S., Boubekeur, N., 2019. Removal of methylene blue using activated carbon prepared from date stones activated with NaOH. *Global Nest Journal* 21, 374–380.
- Gong, R., Li, M., Yang, C., Sun, Y., Chen, J., 2005. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. *Journal of Hazardous Materials* 121, 247–250.
- Grylewicz, A., Mozia, S., 2020. Polymeric mixed-matrix membranes modified with halloysite nanotubes for water and wastewater treatment: A review. *Separation and Purification Technology* 256, 117827.
- Hayati, B., Maleki, A., Najafi, F., *et al.*, 2018. Heavy metal adsorption using PAMAM/CNT nanocomposite from aqueous solution in batch and continuous fixed bed systems. *Chemical Engineering Journal* 346, 258–270.
- Hokkanen, S., Bhatnagar, A., Sillanpää, M., 2016. A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Research* 91, 156–173.
- Hosseinzadeh, M., 2018. Removal of heavy metal ions from aqueous solutions using modified poly (styrene-alt-maleic anhydride) copolymer as a chelating resin. *Russian Journal of Applied Chemistry* 91, 1984–1993.
- Huang, Y., Zeng, M., Ren, J., *et al.*, 2012. Preparation and swelling properties of graphene oxide/poly (acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 401, 97–106.
- Huang, Y., Li, J., Chen, X., Wang, X., 2014. Applications of conjugated polymer based composites in wastewater purification. *RSC Advances* 4, 62160–62178.
- Kumar, R., Sharma, R.K., Singh, A.P., 2017. Cellulose based grafted biosorbents-Journey from lignocellulose biomass to toxic metal ions sorption applications – A review. *Journal of Molecular Liquids* 232, 62–93.
- Kumar, R., Sharma, R.K., Singh, A.P., 2018. Removal of organic dyes and metal ions by cross-linked graft copolymers of cellulose obtained from the agricultural residue. *Journal of Environmental Chemical Engineering* 6, 6037–6048.
- Kumar, R., Ansari, M.O., Alshahrie, A., *et al.*, 2019. Adsorption modeling and mechanistic insight of hazardous chromium on para toluene sulfonic acid immobilized-polyaniline@ CNTs nanocomposites. *Journal of Saudi Chemical Society* 23, 188–197.

- Lagergren, S.K., 1898. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24, 1–39.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society* 40, 1361–1403.
- Li, R., Liu, L., Yang, F., 2013. Preparation of polyaniline/reduced graphene oxide nanocomposite and its application in adsorption of aqueous Hg (II). *Chemical Engineering Journal* 229, 460–468.
- Liu, L., Fan, S., Li, Y., 2018. Removal behavior of methylene blue from aqueous solution by tea waste: Kinetics, isotherms and mechanism. *International Journal of Environmental Research and Public Health* 15, 1321.
- Liu, Q., Zhou, Y., Lu, J., Zhou, Y., 2020. Novel cyclodextrin-based adsorbents for removing pollutants from wastewater: A critical review. *Chemosphere* 241, 125043.
- Liu, Y., Xu, H., Yang, S.-F., Tay, J.-H., 2003. A general model for biosorption of Cd^{2+} , Cu^{2+} and Zn^{2+} by aerobic granules. *Journal of Biotechnology* 102, 233–239.
- Lonappan, L., Rouissi, T., Das, R.K., *et al.*, 2016. Adsorption of methylene blue on biochar microparticles derived from different waste materials. *Waste Management* 49, 537–544.
- Mahmud, H.E., Kassim, A., Zainal, Z., Yunus, W.M.M., 2006. Fourier transform infrared study of polypyrrole-poly (vinyl alcohol) conducting polymer composite films: Evidence of film formation and characterization. *Journal of Applied Polymer Science* 100, 4107–4113.
- Mahmud, H.N.M.E., Obidul Huq, A.K., Binti Yahya, R., 2016. The removal of heavy metal ions from wastewater/aqueous solution using polypyrrole-based adsorbents: A review. *RSC Advances* 6, 14778–14791.
- Mallakpour, S., Behranvand, V., 2017. Application of recycled PET/carboxylated multi-walled carbon nanotube composites for Cd^{2+} adsorption from aqueous solution: A study of morphology, thermal stability, and electrical conductivity. *Colloid and Polymer Science* 295, 453–462.
- Mashkoor, F., Nasar, A., 2020. Carbon nanotube-based adsorbents for the removal of dyes from waters: A review. *Environmental Chemistry Letters*. 1–25.
- Mishra, A.K., Ramaprabhu, S., 2011. Removal of metals from aqueous solution and sea water by functionalized graphite nanoplatelets based electrodes. *Journal of Hazardous Materials* 185, 322–328.
- Nasir, A., Masood, F., Yasin, T., Hameed, A., 2019. Progress in polymeric nanocomposite membranes for wastewater treatment: preparation, properties and applications. *Journal of Industrial and Engineering Chemistry* 79, 29–40.
- Oukil, S., Bali, F., Halliche, D., 2019. Adsorption and kinetic studies of methylene blue on modified HUSY zeolite and an amorphous mixture of γ -alumina and silica. *Separation Science and Technology*. 1–17.
- Pan, N., Deng, J., Guan, D., Jin, Y., Xia, C., 2013. Adsorption characteristics of Th (IV) ions on reduced graphene oxide from aqueous solutions. *Applied Surface Science* 287, 478–483.
- Pandey, N., Shukla, S., Singh, N., 2017. Water purification by polymer nanocomposites: An overview. *Nanocomposites* 3, 47–66.
- Qu, X., Brame, J., Li, Q., Alvarez, P.J., 2012. Nanotechnology for a safe and sustainable water supply: Enabling integrated water treatment and reuse. *Accounts of Chemical Research* 46, 834–843.
- Petre, R., Petrea, N., Epure, G., Zecheru, T., 2015. Polymer composite materials and applications for chemical protection equipments. In: *Proceedings of the International Conference Knowledge-based Organization, Sciendo*, pp. 873–877.
- Ramesha, G., Kumara, A.V., Muralidhara, H., Sampath, S., 2011. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. *Journal of colloid and interface science* 361, 270–277.
- Randelović, S., Zarubica, A.R., Purenović, M.M., 2012. New composite materials in the technology for drinking water purification from ionic and colloidal pollutants. In: Hu, N. (Ed.), *Composites and Their Applications*. IntechOpen.
- Rao, G.P., Lu, C., Su, F., 2007. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Separation and Purification Technology* 58, 224–231.
- Redlich, O., Peterson, D.L., 1959. A useful adsorption isotherm. *Journal of Physical Chemistry* 63, 1024.
- Ren, X., Li, J., Tan, X., Wang, X., 2013. Comparative study of graphene oxide, activated carbon and carbon nanotubes as adsorbents for copper decontamination. *Dalton Transactions* 42, 5266–5274.
- Ruthven, D.M., 1984. *Principles of Adsorption and Adsorption Processes*. John Wiley & Sons.
- Sahu, N., Rawat, S., Singh, J., *et al.*, 2019. Process optimization and modeling of methylene blue adsorption using zero-valent iron nanoparticles synthesized from sweet lime pulp. *Applied Sciences* 9, 5112.
- Senthilkumar, S., Varadarajan, P., Porkodi, K., Subburaam, C., 2005. Adsorption of methylene blue onto jute fiber carbon: Kinetics and equilibrium studies. *Journal of Colloid and Interface Science* 284, 78–82.
- Sips, R., 1948. On the structure of a catalyst surface. *The Journal of Chemical Physics* 16, 490–495.
- Tan, I., Hameed, B., Ahmad, A., 2007. Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal* 127, 111–119.
- Tan, I., Ahmad, A., Hameed, B., 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials* 154, 337–346.
- Teow, Y.H., Mohammad, A.W., 2019. New generation nanomaterials for water desalination: A review. *Desalination* 451, 2–17.
- Tiwari, J.N., Mahesh, K., Le, N.H., *et al.*, 2013. Reduced graphene oxide-based hydrogels for the efficient capture of dye pollutants from aqueous solutions. *Carbon* 56, 173–182.
- Tofighy, M.A., Mohammadi, T., 2010. Salty water desalination using carbon nanotube sheets. *Desalination* 258, 182–186.
- Tofighy, M.A., Mohammadi, T., 2011. Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. *Journal of Hazardous Materials* 185, 140–147.
- Tofighy, M.A., Mohammadi, T., 2012. Nitrate removal from water using functionalized carbon nanotube sheets. *Chemical Engineering Research and Design* 90, 1815–1822.
- Tofighy, M.A., Mohammadi, T., 2014. Methylene blue adsorption onto granular activated carbon prepared from Harmal seeds residue. *Desalination and Water Treatment* 52, 2643–2653.
- Tofighy, M.A., Mohammadi, T., 2015. Copper ions removal from water using functionalized carbon nanotubes–mullite composite as adsorbent. *Materials Research Bulletin* 68, 54–59.
- Tofighy, M.A., Mohammadi, T., 2019. Barrier, diffusion, and transport properties of rubber nanocomposites containing carbon nanofillers. In: Yaragalla, S., Mishra, R.K., Thomas, S., Kalirikkal, N., Maria, H.J. (Eds.), *Carbon-Based Nanofiller and Their Rubber Nanocomposites*. Elsevier, pp. 253–285.
- Tofighy, M.A., Mohammadi, T., 2020. Chapter 5 – Carbon nanotubes-polymer nanocomposite membranes for pervaporation. In: Thomas, S., George, S.C., Jose, T. (Eds.), *Polymer Nanocomposite Membranes for Pervaporation: Micro and Nano Technologies*. Elsevier, pp. 105–133.
- Tran, H.N., You, S.-J., Chao, H.-P., 2016. Effect of pyrolysis temperatures and times on the adsorption of cadmium onto orange peel derived biochar. *Waste Management & Research* 34, 129–138.
- Vagheti, J.C., Lima, E.C., Royer, B., *et al.*, 2009. Pecan nutshell as biosorbent to remove Cu (II), Mn (II) and Pb (II) from aqueous solutions. *Journal of Hazardous Materials* 162, 270–280.
- Vuković, G.D., Marinković, A.D., Čolić, M., *et al.*, 2010. Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chemical Engineering Journal* 157, 238–248.
- Wang, R.-M., Zheng, S.-R., Zheng, Y.G., 2011. *Polymer Matrix Composites and Technology*. Elsevier.
- Wang, X., Liu, Z., Ye, X., *et al.*, 2014. A facile one-step approach to functionalized graphene oxide-based hydrogels used as effective adsorbents toward anionic dyes. *Applied Surface Science* 308, 82–90.
- Wu, K., Yu, J., Jiang, X., 2018. Multi-walled carbon nanotubes modified by polyaniline for the removal of alizarin yellow R from aqueous solutions. *Adsorption Science & Technology* 36, 198–214.
- Xie, Y., He, C., Liu, L., *et al.*, 2015. Carbon nanotube based polymer nanocomposites: biomimic preparation and organic dye adsorption applications. *RSC Advances* 5, 82503–82512.

- Yang, S.-T., Chen, S., Chang, Y., *et al.*, 2011. Removal of methylene blue from aqueous solution by graphene oxide. *Journal of Colloid and Interface Science* 359, 24–29.
- Yang, Y., Xie, Y., Pang, L., *et al.*, 2013. Preparation of reduced graphene oxide/poly (acrylamide) nanocomposite and its adsorption of Pb (II) and methylene blue. *Langmuir* 29, 10727–10736.
- Yang, Z., Ma, X.-H., Tang, C.Y., 2018. Recent development of novel membranes for desalination. *Desalination* 434, 37–59.
- Yao, T., Wang, C., Wu, J., *et al.*, 2009. Preparation of raspberry-like polypyrrole composites with applications in catalysis. *Journal of Colloid and Interface Science* 338, 573–577.
- Yu, T., Xue, Z., Zhao, X., Chen, W., Mu, T., 2018. Green synthesis of porous β -cyclodextrin polymers for rapid and efficient removal of organic pollutants and heavy metal ions from water. *New Journal of Chemistry* 42, 16154–16161.
- Yue, X., Jiang, F., Zhang, D., Lin, H., Chen, Y., 2017. Preparation of adsorbent based on cotton fiber for removal of dyes. *Fibers and Polymers* 18, 2102–2110.
- Yue, Y., Wang, X., Wu, Q., Han, J., Jiang, J., 2019. Assembly of polyacrylamide-sodium alginate-based organic-inorganic hydrogel with mechanical and adsorption properties. *Polymers* 11, 1239.
- Zahid, M., Rashid, A., Akram, S., Rehan, Z., Razzaq, W., 2018. A comprehensive review on polymeric nano-composite membranes for water treatment. *Journal of Membrane Science & Technology* 8, 1–20.
- Zarghami, S., Tofighy, M.A., Mohammadi, T., 2015. Adsorption of zinc and lead ions from aqueous solutions using chitosan/polyvinyl alcohol membrane incorporated via acid-functionalized carbon nanotubes. *Journal of Dispersion Science and Technology* 36, 1793–1798.
- Zhang, H., Li, Y., Wang, P., *et al.*, 2019. Synthesis of β -cyclodextrin immobilized starch and its application for the removal of dyestuff from waste-water. *Journal of Polymers and the Environment* 27, 929–941.
- Zhu, W., Liu, L., Liao, Q., *et al.*, 2016. Functionalization of cellulose with hyperbranched polyethylenimine for selective dye adsorption and separation. *Cellulose* 23, 3785–3797.

Nanomaterial-Incorporated Polymer Composites for Industrial Effluent: From Synthesis to Application

Yousef Tamsilian, Shahid Chamran University of Ahvaz, Ahvaz, Iran

Mahsa Shirazi, Sharif University of Technology, Tehran, Iran

Gholamreza Masoudi Rad, Petroleum University of Technology, Ahvaz, Iran

© 2021 Elsevier Inc. All rights reserved.

Nomenclature

BPA Bisphenol A

CNT Carbon Nanotube

COD Chemical Oxygen Demand

CVD Chemical Vapor Deposition

E. coli Escherichia coli

FO Forward Osmosis

GO Graphene Oxide

HDPE High-density Polyethylene

LDH Layered Double Hydroxide

LDPE Low-density Polyethylene

MO Methyl Orange

MB Methylene Blue

MMT Montmorillonite

MWCNT Multi-walled Carbon Nanotube

NP Nanoparticle

PANI Polyaniline

PS Poly(Styrene)

PEG Polyethylene Glycol

PET Polyethylene Terephthalate

PEI Polyethylenimine

PNC Polymer Nanocomposite

PCNC Polymer-clay Nanocomposites

PSF Polysulfone

PVA Polyvinyl Alcohol

RGO Reduced Graphene Oxide

SWCNT Single-walled Carbon Nanotube

Introduction

A huge amount of wastewater contaminants with various toxic pollutants (ex. heavy metals and metalloids, pesticides, phenols, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and polybrominated diphenyl ethers) are annually released into the environment as a result of rapid industrialization and harmful anthropogenic activities. The disposal of such effluents in the environment without any treatment is a serious threat to the plant, animals, and human health along with the waste of valuable resources. Some of the commonly used techniques for the treatment of industrial effluents are precipitation, adsorption, membrane filtration, ion exchange, ion flotation, reverse osmosis, complexation, photo- and electro-catalysis, and electrodialysis (Fu and Wang, 2011; Barakat, 2011; Zhu *et al.*, 2016; Szczepanik, 2017). Despite the widespread practical application of these methods, the complex operation, high capital and energy costs, low selectivity, slow separation kinetics, sludge formation, unproven performance in large-scale implementation, inefficient treatment of wastes with low contaminant concentration or complex structure contaminant, and the risk of secondary pollution limit their application in large-scales. Among the aforementioned methods, adsorption is one of the most efficient technologies for the wastewater purification (Raval *et al.*, 2016; Singh *et al.*, 2018). Some of the common types of organic and inorganic adsorbents previously used in wastewater treatments are natural and activated zeolites (Singh *et al.*, 2018; Bosso and Enzweiler, 2002; Inglezakis *et al.*, 2003; Syafalni *et al.*, 2014), natural and modified clay minerals (Fan *et al.*, 2009; Rusmin *et al.*, 2015; Olu-Owolabi *et al.*, 2017; Mukhopadhyay *et al.*, 2017; Kumararaja *et al.*, 2018; Yadav *et al.*, 2019; Han *et al.*, 2019), activated carbons (Singh *et al.*, 2018; Mirmohseni *et al.*, 2012; Nethaji *et al.*, 2013; Ahmed, 2017), biochar (Mohan *et al.*, 2014; Xie *et al.*, 2015; Shaheen *et al.*, 2019; Palansooriya *et al.*, 2020; Premarathna *et al.*, 2019), agricultural waste (Anastopoulos and Kyzas, 2014; Bhatnagar *et al.*, 2015; Shakoar *et al.*, 2018; Ahmad and Danish, 2018), industrial waste and sludge materials (Bhatnagar and Sillanpää, 2010; Zhao *et al.*, 2016; Anastopoulos *et al.*, 2017), and polymeric resins (Singh *et al.*, 2018; Rivas and Munoz, 2009; Gandhi *et al.*, 2010). A proper selection of adsorbents depends on the adsorption efficiency, benefit to cost ratio, and the specificity of a particular toxic agent. Among the mentioned adsorbents, natural clay minerals are intensively used due to their easy availability and cost-effectivity (Mukhopadhyay *et al.*, 2017), however, the low surface area, low potential of removing micro-pollutants, and lack of standard protocols of regeneration and recovery in aqueous systems, limit their usage (Unuabonah *et al.*, 2018; Sarkar *et al.*, 2019; Unuabonah and Taubert, 2014; Bhattacharyya and Gupta, 2008). Polymeric resin adsorbents have the potential of overcoming the drawbacks of clay minerals; however, they possess some negative characteristics including pH dependency, high cost, poor water wettability, and particle size sensitivity, which limit their widespread applications (Unuabonah and Taubert, 2014). Considering the advantages and disadvantages of the nano and polymeric adsorbents, researchers have paid attention to the development of polymer nanocomposites (PNCs) to combine their beneficial features and overcome the limitation of using them individually.

Polymer nanocomposites (PNCs) in which, polymer serves as the matrix while the organic or inorganic material acts as the nanofiller (Sengodu and Deshmukh, 2015) have gained significant industrial and scientific attractions, because of their unique physiochemical properties, emerging from the combination of polymer and nanomaterial, that cannot be obtained with individual components acting alone. PNCs exhibit enhanced functionalities and related advantages rather than native polymers including cost-

effectivity, environmental stability, permeability (for water and gases), electrical conductivity, high strength, high elastic modulus, large surface to volume ratio, large flame retardancy, and enhanced mechanical, thermal, optoelectronic, and magnetic properties (Safdari and Al-Haik, 2013; Rafiee *et al.*, 2009; Mansor and Akop, 2020; Kumar *et al.*, 2013). These tremendous properties have made PNCs good choices for their use in diversified industrial fields including water and wastewater treatments.

The purpose of this article is to focus on the types of PNCs that are applicable in industrial effluent treatments followed by a detailed explanation of their fabrication methods (melting-based methods, solvent-based methods, and in-situ methods) and their implementation for effluent applications (membranes, adsorbents, photocatalyst, disinfectants, and sensors).

Types of Polymer Nanocomposites Relevant for Effluent Processing

PNCs are a combination of a polymer matrix (natural/synthetic) and a filler (organic/inorganic). The fillers have usually one dimension in the nanoscale (clay minerals), two dimensions in the nanoscale (carbon nanotubes (CNTs), nanofibers, nanowires, etc.), or three dimensions in the nanoscale (silica nanoparticles (NPs), etc.) (Azeez *et al.*, 2013; Soetaredjo *et al.*, 2018).

As noted earlier, adsorption is one of the most efficient and cost-effective processes for the purification of wastewater (Singh *et al.*, 2018) and based on the recent studies, nanoclays have earned more attraction for adsorbing various pollutants from the wastewater in comparison with other commercially available adsorbents. This is because of their wide availability, relatively low cost, relatively low environmental impact, and superior surface sorption mechanism (Guo *et al.*, 2018). Different clay minerals can be used as fillers to enhance the absorption of contaminants such as metallic ions and dyes. The adsorption properties of clay minerals can often be improved through mixing with other materials such as polymer, forming polymer-clay nanocomposites (PCNCs) (Awasthi *et al.*, 2019). The clay minerals used for the development of PCNCs are crystalline structures mainly composed of tetrahedral (SiO_4)⁴⁻ and octahedral ($\text{AlO}_3(\text{OH})_3$)⁶⁻ sheets (Mukhopadhyay *et al.*, 2020). They are mainly divided into seven groups, namely kaolinite group (e.g., kaolinite, halloysite, serpentine) (Miranda-Trevino and Coles, 2003), non-expanding group (e.g., mica and illite), limited expanding group (e.g., vermiculite), strongly expanding group (e.g., montmorillonite (MMT)), uncharged group (e.g., pyrophyllite and talc), 2:1:1 group (e.g., chlorites), and fibrous-layered silicates (e.g., palygorskite and sepiolite) (Lee and Tiwari, 2012; Mukhopadhyay *et al.*, 2020).

One of the most essential clay minerals for the development of PCNCs is MMT in smectite groups that belong to the family of 2:1 phyllosilicate. They are composed of two silica-based tetrahedral sheets with water molecules within the interlayer sheets and are easily available for incoming contaminants (Rajapaksha *et al.*, 2019). MMT has a hydrophilic nature, so it is required to modify its surface to make it organophilic/hydrophobic, before preparation of PNCs. Different organic cations are widely used as surface modifiers of MMT clays such as silane and aluminum salts (Huskić *et al.*, 2013; Khajepour *et al.*, 2015; Davis *et al.*, 2003).

Another widely used nanofiller for the preparation of polymeric nanocomposites is carbon nanotubes (CNTs). Carbon-based nanomaterials were first discovered in 1988 with the discovery of buckyball, a molecule made of pure carbon with ball shape, by Kroto *et al.* (1985). Another important discovery was reported by Iijima in 1991, as he reported the discovery of CNTs, a tubular form of carbon (Iijima, 1991). There are many ways for the preparation of CNTs, the most widely used ones are chemical vapor deposition (CVD), sol-gel method, arc discharge method, laser ablation method, and flame synthesis (Khare and Bose, 2005). CNTs that can be used as fillers of PNCs are mainly divided into two groups of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), based on the number of graphite layers on the wall of the CNTs (Rahmandoust and Ayatollahi, 2016). CNTs have been used for a variety of applications due to their excellent thermo-mechanical and electrical properties (Basheer *et al.*, 2020). Dispersion of CNTs into the polymer matrices increases the adsorption performance of PNCs (Shabaan *et al.*, 2020; Zhuang *et al.*, 2020; Rodríguez and Leiva, 2020; Bassyouni *et al.*, 2020). Bin-Dahman *et al.* investigated the batch adsorption performance of a hybrid material, oxidizing CNT grafted with polyethylene glycol (PEG) (CNT/PEG), for the removal of phenol from wastewater. They found that the adsorption performance of CNT/PEG under optimum conditions was high ($\approx 100\%$) for phenol removal at a contact time of 30 min. They also demonstrated that the prepared hybrid material (CNT/PEG) was an efficient adsorbent for removal of phenol from water as well as for simultaneous removal of phenol with metallic ions such as Cu, Hg, Cr, Fe, Co, Ni, Al, and Pb from industrial effluents (Bin-Dahman and Saleh, 2020). Another important application of polymer grafted CNTs is the water/oil separation membranes. Gu *et al.* developed a simple and robust method to fabricate Janus polymer/CNT hybrid membranes for oil/water separation. They prepared a membrane by dispensing hydrophobic poly (styrene) (PS) and hydrophilic poly(N, N-dimethylaminoethyl methacrylate) (PDMAEMA) that were grafted from different sides of the photoactive CNT membranes via self-initiated photo grafting and photopolymerization (SIPGP). The produced membranes demonstrated excellent selectivity for the removal of oil from water. They also separated both surfactant-stabilized oil-in-water and water-in-oil emulsions effectively, attributed to their anisotropic wettability (Gu *et al.*, 2014).

In recent years, 2D carbon-based nanomaterials such as graphene, graphene oxide (GO), and reduced graphene oxide (RGO) have gained the attention of scientists to use them as fillers for the preparation of PNCs, as the adsorbent for efficient removal of contaminants from wastewater (Yan *et al.*, 2016). These materials possess unique properties such as large surface area, high porosity range, exceptional mechanical strength, and abundant oxygen-containing functional groups such as hydroxyl, carbonyl, epoxy, and carboxylic groups which make them suitable for the fabrication of membranes. Besides, GO can be synthesized from low cost and available graphite (Bera and Maji, 2017). The RGO that contains very low oxygen-containing functional groups is obtained by simple reduction of GO, compatible with less polar or nonpolar organic polymers. As an adsorbent of organic dyes

from wastewater, GO/polyethylenimine (PEI) hydrogels can be effectively used. Graphene-based polymeric nanocomposites can also be used to remove harmful metal ions such as lead (II) and chromium (VI) from wastewater. The graphene-based polymeric nanocomposite membranes such as polysulfone (PSF)/graphene and cellulose/graphene composite membranes are other important adsorbents that have been recently used for the purification of wastewater (Bera and Maji, 2017).

Other nanomaterials that have been widely used in the preparation of polymeric nanocomposites for wastewater treatment are ZnO (Sheikh *et al.*, 2020; Nerkar *et al.*, 2018), porous silica (Betiha *et al.*, 2020), Fe₃O₄ (Badrudodoza *et al.*, 2013), hydroxyapatite (Pai *et al.*, 2021), TiO₂ (Vellaichamy *et al.*, 2017; Hou *et al.*, 2017), and Zr (Gupta *et al.*, 2014) NPs. Gupta *et al.* investigated the adsorption of methylene blue (MB) dye from water systems using novel polyaniline zirconium (IV) silicophosphate (PANI-ZSP) nanocomposite material. They prepared the PNC material by mixing polyaniline (PANI) polymer with the inorganic counterpart (ZSP) using the sol-gel method at 0–1 pH. Their results indicated the PANI-ZSP nanocomposite as an efficient adsorbent for the removal of MB dye from wastewater (Gupta *et al.*, 2014). In another paper, Vellaichamy *et al.* synthesized a new polymeric nanocomposite, PANI/manganese dioxide/titanium dioxide (PANI/MnO₂/TiO₂), using an in-situ method for reduction of toxic Cr⁶⁺ present in the wastewater to Cr³⁺. They claimed that the prepared nanocomposite exhibited a superior catalytic activity in the conversion of toxic Cr⁶⁺ to benign Cr³⁺ in comparison with other nanocomposite materials reported with an excellent conversion of 99.9% (Vellaichamy *et al.*, 2017).

Another classification of PNCs for application in the treatment of effluents is based on polymer matrices. Polymeric materials are divided into two groups of natural and synthetic polymers. Natural polymers can occur in plants or animals while synthetic polymers are derived from petroleum oil and can be artificially produced in laboratories (Shrivastava, 2018).

Different types of natural polymers are used as polymer matrices for wastewater treatment, such as cellulose (Shi *et al.*, 2020), starch (Ahmad *et al.*, 2020), chitin (Perez *et al.*, 2020), chitosan (Rani *et al.*, 2020), gelatin (Ahmad *et al.*, 2020), alginate (Esmat *et al.*, 2017), pectin (Gupta *et al.*, 2012) and guar gum (Pathania *et al.*, 2016; Patra *et al.*, 2017; Zahran and Marei, 2019; Nasrollahzadeh *et al.*, 2021).

Shi *et al.* developed Ag–ZnO/cellulose nanocomposites via tunable cellulose size for improving photocatalytic performance. They controlled the diameter distribution of cellulose by grinding them 10, 20, and 30 times which resulted in average fibril diameters of 130, 64, 42 nm, respectively. Their PNC exhibited excellent photocatalyst activity for the degradation of methyl orange (MO) present in wastewater. Besides, their PNC demonstrated outstanding stability and reusability even after 10 cycles of use (Shi *et al.*, 2020).

In another study, Azizi synthesized Fe₃O₄/cellulose nanocomposites for the removal of metronidazole from aquatic solutions by the adsorption method. They evaluated the adsorption capacity of their PNC by optimizing four important parameters including pH, initial concentration of metronidazole, amount of nanocomposite, and contact time. Their results indicated that the PNC had a high removal efficiency of 97.04% at the optimal operating conditions, demonstrating it as a suitable adsorbent for environmental applications (Azizi, 2020).

Rani *et al.* synthesized iron-oxide-based chitosan-nanocomposites via green route for photo-oxidative degradation of polycyclic-aromatic-hydrocarbons (PAHs) such as anthracene (ANTH) and phenanthrene (PHEN). The highest degradation was observed for ZnFe₂O₄-CS (ANTH: 95%, PHE: 92%) followed by CuO-Fe₂O₃-CS (93%, 90%), NiFe₂O₄-CS (90%, 88%), Co₂O₃-Fe₃O₄-CS (88%, 85%) and FeCr₂O₄-CS (83%, 81%), respectively. They indicated the insight on preparing effective, green, reusable ($n = 10$), stable nanocomposites for the removal of carcinogenic PAHs from wastewater (Rani *et al.*, 2020).

Perez *et al.* synthesized a low-cost and regenerable composite based on chitin/bentonite for the adsorption of pollutants such as trimethoprim (TMP) present in wastewaters. They conducted different characterization tests such as ATR-FTIR, XRD, DSC, and TGA, all of which revealed the intercalation of the chitin macromolecules into the bentonite interlayer. The maximum adsorption capacity of TMP was 67 mg/g, indicated by Langmuir Isotherm. After three regeneration cycles, the sectioned composite reached around 100% adsorption capacity (Perez *et al.*, 2020).

Polar and non-polar synthetic polymer matrices can provide some properties that make PNCs suitable for application in different wastewater treatment such as membrane filtration, adsorption, photocatalyst, microbial and control agent, and sensing and monitoring of contaminants. Some examples of synthetic polymers are high-density polypropylene (HDPE) (Amini *et al.*, 2017), low-density polyethylene (LDPE) (Romero-Sáez *et al.*, 2017), polyvinyl alcohol (PVA) (Isawi, 2020; Mahdavinia *et al.*, 2017), PEG (Khalid *et al.*, 2018; Saeedi-Jurkuyeh *et al.*, 2020), polyacrylic acid (Rafei *et al.*, 2016; Sun *et al.*, 2015), polyesteramide (PEA) (Soetaredjo *et al.*, 2018), and polypyrrole (PPy) (Aigbe *et al.*, 2018).

Aigbe *et al.* developed different PNCs by dispersion of various nanofillers such as zinc oxide (ZnO), silicon dioxide (SiO₂), titanium dioxide (TiO₂), GO, and aluminum oxide (Al₂O₃) into the polyethersulfone polymer matrix to produce a mixed-matrix membrane. They also compared the effect of different nanofillers and the efficiency of the developed membranes for the removal of rhodamine B (RhB) dye from textile wastewaters. Based on their observations, all of the membranes exhibited high RhB removal efficiency of 91.96%–96.92% (Aigbe *et al.*, 2018).

The removal of brilliant green dye from the wastewater was investigated by Shirsath *et al.*, using a poly(acrylic acid) hydrogel composite (PAA-K hydrogel) prepared by incorporation of kaolin clay. They reported that the PNC had high dye adsorption at the optimum condition with a pH of 7, a temperature of 35 °C, an initial dye concentration of 30 mg/L, and hydrogel loading of 1 g (Shirsath *et al.*, 2013).

Shokri *et al.* developed fouling resistant and highly permeable polyvinyl chloride (PVC) ultra-filtration membranes by dispersing different amounts of natural and modified MMTs with folic acid (Mt-FA). Modification of MMT with folic acid resulted in better dispersion of MMT in the polymer matrix. Their results revealed that all PNC membranes showed hydrophilicity and roughness compared with neat PVC. Besides, their results demonstrated that the incorporation of MMT NPs into the polymer matrix enhanced the pure water flux, porosity, mechanical strength, and reusability of the membranes (Shokri *et al.*, 2020).

Fabrication Methods of Polymer Nanocomposites

After selecting the desired NPs with an acceptable level of compatibility with the polymer matrix to develop a PNC, it is necessary to choose the best fabrication method to obtain a uniform distribution and dispersion of NPs in the polymer matrix, without any aggregation. The common fabrication methods of PNCs are divided into three main categories of melting-based, solvent-based, and in-situ methods, each of them has multiple subcategories described as follows.

Considering the purpose of this article to focus on the PNCs which are applicable in the industrial effluent treatments, all of the fabrication methods of the PNCs are given in this section with a detailed explanation since there is no significant difference between the synthesis methods of the efficient PNCs for effluent treatments and that of the inefficient ones. In the present section, we have tried to cover all of the fabrication methods, although some of them may not be used in the case of the special PNCs with the application in effluent processing, to ensure mentioning the fabrication methods of the applicable PNCs that might not be mentioned in this work. Then in Section “Implementation of Polymer Nanocomposites for Effluent Applications”, the applicable PNCs in the treatment of effluents along with their method of fabrication are introduced and for more details about synthesis methods, it is required to refer to the present section.

Melting-Based Methods

Melt blending method

In this method, the polymer powder is melted to obtain a viscous solution and the nanofillers are then added into the polymer solution and dispersed under a high shear rate and high-temperature diffusion to reduce the size of possible agglomerates, using single or twin-extruders (Mallakpour and Naghdi, 2018). The strain applied to the NPs by the polymer depends on the polymer molecular weight and weight distribution. First, by applying the high shear rates, the large agglomerates are breakdown and form smaller ones that dispersed within the polymer matrix (Fig. 1a). The transferred strain from polymer to the new smaller agglomerates leads to a stronger shearing that breaks the agglomerates into the individual particles, which strongly depends on the time and chemical affinity between the polymer and NPs' surface (Fig. 1b) (Mistretta *et al.*, 2014). Finally, the individual NPs are separated and diffused in the melted polymer matrix (Fig. 1c). The final shape of the nanocomposites can be fabricated by compression molding, injection molding, or fiber production techniques. The melt blending method is one of the popular fabrication methods of PCNCs. Some of the common advantages of this technique are its cost-effectivity, ecofriendly, high heat stability, good mechanical properties, and high compatibility with industrial operations such as extrusion and injection molding to be commercialized (Mallakpour and Marefatpour, 2014; Dong *et al.*, 2012; Mallakpour and Naghdi, 2018). The big limitation of this method is the need for high temperature which may have a detrimental effect on the polymer matrix and also on the modified surface of the nanofillers. Besides, the interaction between polymer and NPs is not easy to control in this method, and consequently, it may be difficult to obtain a good dispersion of the nanofillers (Fischer, 2003; Tanahashi, 2010).

Melt mixing method

Similar to the previous, the polymer is melted in this method. To achieve an acceptable dispersion of nanofillers in the melt solution, a high-shear mixing and a proper choice of polymer and compatibilizer/surfactant are required. The purpose of using a compatibilizer is to control the melt solution viscosity since the addition of nanofillers significantly increases its viscosity. The melt mixing method is one of the appropriate fabrication methods of insoluble or immiscible polymers (Goyal, 2017). Some of the

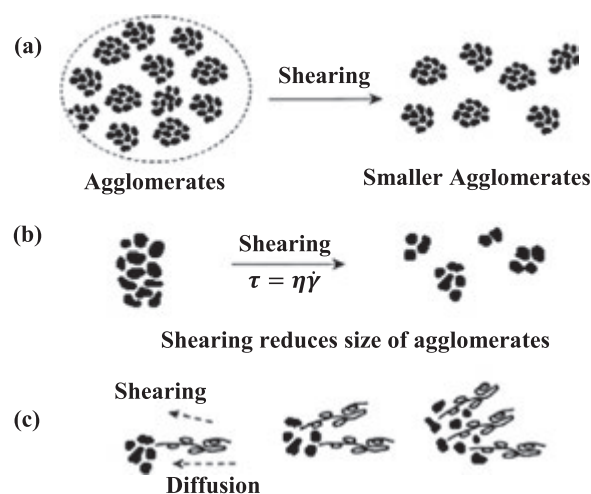


Fig. 1 Effect of shear stress on NP dispersion during melt blending. Reproduced from de Oliveira, A.D., Beatrice, C.A.G., 2018. Polymer nanocomposites with different types of nanofiller. In: Sivasankaran, S. (Ed.), Nanocomposites-Recent Evolutions. IntechOpen. pp. 103–104.

main benefits of this technique are cost-effectivity, ecofriendly, simplicity, and availability. Similar to the melt blending method, the big limitation of this technique is the usage of high temperatures. Besides, despite the positive effect of high shear mixing on achieving good dispersion of nanofillers, it reduces the aspect ratio of the nanofillers, having a negative effect on enhancing the nanocomposite properties. Consequently, the choice of a proper value of shear rate to obtain a good dispersion without any negative effect on the aspect ratio is still a challenge of this method (Feng *et al.*, 2014). Furthermore, it is usually required to chemically treat the surface of the nanofillers to obtain proper compatibility with the polymer matrix and good dispersion.

Melt compounding method

In this method, nanofillers are added to the polymer melt solution above the glass transition temperature (T_g). A high shear rate is induced in the polymer melt by viscous drag to breakdown the nanofiller aggregates and obtain a uniform homogeneous dispersion in the polymer matrix. Melt compounding is a simple and cost-effective method to fabricate high-performance PNCs. The critical threshold shear stress value that is necessary for breaking down the nanofillers agglomerates is the main factor to control the dispersion state of the fillers in the melt-compounding method.

Melt intercalation method

In this method, the polymer matrix is annealed at the molten temperature, the fillers are added and the mixture of polymer and nanofillers are kneaded either statically or under shear to reach a uniform distribution. Dispersion of nanofillers in the polymer matrix occurs in four steps: (1) wetting of the initial nanofillers agglomerates by the polymer, (2) infiltration of the polymer chains into the initial agglomerates to weaken them, (3) breaking down and disruption of the agglomerates to reach a smaller one, and (4) dispersion and distribution of individual nanofillers into the polymer matrix. The nanofillers dispersion depends on different factors such as processing conditions, surface modification of the nanofillers, and the compatibility between the fillers and polymer matrix. The melt intercalation is a typical fabrication method of thermoplastic PNCs and depending on the electrostatic forces among the filler interlayers and the compatibility with the polymer matrix, an intercalated or exfoliated morphology will be formed. Some of the common advantages of this method are cost-effectivity, ecofriendly, compatibility with the industrial processes such as extrusion and injection molding, and easy to commercialized. The only limitation is the usage of high temperatures that can damage the polymer chains and the modified surface of the nanofillers. As an instance, the surface of organoclay nanofillers that is usually modified with alkyl ammonium decomposes at temperatures higher than 140 °C, while the required temperature of melt intercalation is in the range of 190–220 °C. The usage of more thermally stable surface modifiers along with operating at lower temperatures are some of the proposed methods to address this limitation.

Solvent-Based Methods

Solvent method

In this method, the NPs and polymer are dispersed in a solvent and co-solvent, respectively. The dispersion of nanofillers in the solvent is conducted by sonication to breakdown the nanofillers aggregates. The resulting nanocomposite is then recovered from the solvent via solvent evaporation/coagulation. The induced shear rate on the polymer matrix in this method is lower than the case of the melt compounding method (Jannapu Reddy, 2010).

Solution method

In this method, both polymer and nanofillers are dispersed in a common solvent, despite the solvent method in which a solvent and a co-solvent are required. The resulting nanocomposite is then recovered from the solvent by filtration, precipitation, or film casting. Some of the most common polymers that can be dissolved in organic solvents are polycarbonate, polystyrene, polymethylmethacrylate (PMMA), and PVA. Although the solution method is a simple process, it requires a large amount of solvent that may be dangerous for the environment (Goyal, 2017).

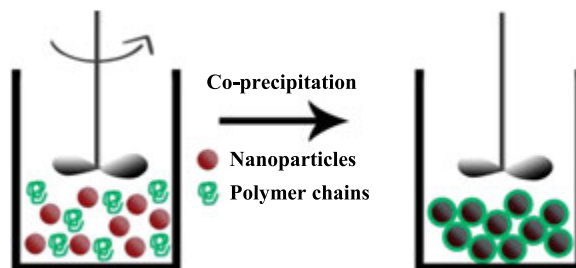


Fig. 2 Schematic illustration of the solution blending method. Reproduced from de Oliveira, A.D., Beatrice, C.A.G., 2018. Polymer nanocomposites with different types of nanofiller. In: Sivasankaran, S. (Ed.), Nanocomposites-Recent Evolutions. IntechOpen. pp. 103–104.

Solution blending method

In this method, the polymer and nanofillers are dispersed in an appropriate solvent. The dispersion of nanofillers can be done via different methods of ultrasonic irradiation, magnetic stirring, or shear mixing (Passador *et al.*, 2017; Naz *et al.*, 2016). The NPs will then remain dispersed into the polymer chains after solvent evaporation resulting in a nanocomposite, schematically shown in Fig. 2. The solution blending is a suitable fabricating method for both thermoplastic and thermoset polymers in the case of all nanofillers. Some of the benefits of this method are easy operation and low gas permeability and the main limitation is the usage of expensive solvents, providing problems from both economic and environmental points of view (Kango *et al.*, 2013; Bhattacharya, 2016).

Solution mixing method

In this method, the nanofillers are swollen in a solvent and the polymer is dissolved in a co-solvent. The two solutions are then mixed and the polymer chains intercalate and displace the solvent within the interlayer of the nanofillers. The dispersion of nanofillers in the polymer solution can be occurred by sonication, magnetic stirring, or shear mixing. An intercalated or exfoliated nanocomposite will remain after solvent evaporation (Rane *et al.*, 2018; Gurses, 2015).

Exfoliation adsorption

In this method, which is also called the polymer/prepolymer intercalation from the solution, the layered nanofillers are first swollen and dispersed in a solvent and the polymer is dissolved in a co-solvent. The polymer chains intercalate and displace the solvent within the interlayer of nanofillers and a multilayer structure will be then formed after solvent removal. The driving force behind this method is the entropy gained by solvent desorption, compensating the entropy reduction caused by the confined intercalated chains. The exfoliation adsorption is a common method of fabricating intercalated PNCs based on the water-soluble polymers and the polymers with little or no polarity such as poly(vinyl alcohol), poly(ethylene oxide), poly(vinylpyrrolidone), or poly(acrylic acid). The main limitation of this method is the usage of a large amount of solvent which is environmentally unfriendly (Ray and Okamoto, 2003; Pavlidou and Papaspyrides, 2008). This method can be subdivided into two methods of solution intercalation and in-situ polymerization both of which are described below.

Solution intercalation method

In this method, the layered nanofillers are dispersed in a solvent in which the polymer is also soluble and exfoliated into the single layers. The polymer chains are then adsorbed onto the delaminated sheets and the sheet reassemble after the solvent evaporation, sandwiching the polymer to form an ordered, multilayered structure (Koo, 2006). The general required steps in the solution intercalation method are (1) dispersion of nanofillers in a solvent by agitation, (2) mixing the nanofillers and polymer solutions by agitation, and (3) controlled evaporation of the solvent and/or precipitation of nanocomposite (Shawky *et al.*, 2011).

Emulsion polymerization

In this method, the layered nanofillers are dispersed in an aqueous phase similar to the solution intercalation method and the polymer monomers are dispersed in water with an emulsifier. The monomers are then polymerized with a part of the NP embedded inside the polymer particle and a part adsorbed on the particle surface, forming a nanocomposite.

Sol-gel method

This method is associated with two relation steps; “sol” as a colloidal suspension of solid NPs dispersed in the monomer solution, and “gel” as a three-dimensional interconnecting network formed between phases by polymerization reactions followed by hydrolysis procedure. This three-dimensional network of polymer NPs spreads across the liquid and the polymer acts as a nucleating agent to enhance the growth of layered crystals. As the crystals grow, the polymer seeps between the layers, forming a nanocomposite (Jannapu Reddy, 2010).

In-Situ Methods

In-situ formation

In this method, the dissolved monomers in an aqueous solution are embedded on the sol-gel matrices and organic groups are then introduced via chemical bonds, leading to the in-situ formation of the sol-gel matrix within the polymer and simultaneous generation of a three-dimensional network. During the process, polymer aids the growth of inorganic host crystals and gets trapped within the nanolayers as they grow. This is a common fabrication method of layered double hydroxide (LDH) nanocomposites (Rane *et al.*, 2018).

In situ template synthesis

In this method, the polymer matrix and nanolayers are dissolved in an aqueous solution. By trapping the polymer chains inside the nanolayers, the nanolayers are nucleated and grown on the polymer chains at high temperatures. The main limitation of this method is the high operating temperature which may degrade or decompose the polymer (Khan *et al.*, 2016).

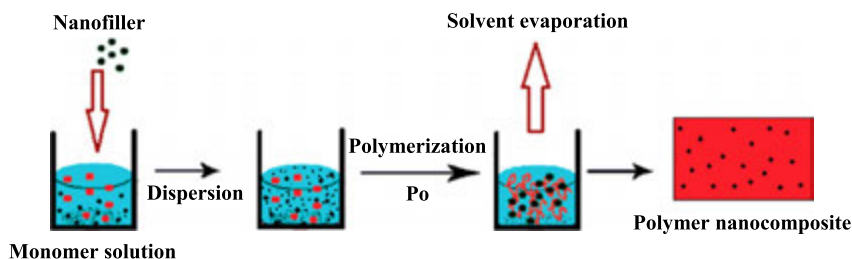


Fig. 3 Schematic illustration of the in situ intercalative polymerization method. Reproduced from de Oliveira, A.D., Beatrice, C.A.G., 2018. Polymer nanocomposites with different types of nanofiller. In: Sivasankaran, S. (Ed.), *Nanocomposites-Recent Evolutions*. IntechOpen. pp. 103–104.

In-situ intercalative polymerization method

In this method, the monomers are dissolved in a solution and by adding the nanofillers, the low molecular weight monomer solution easily seeps in between the nanolayers, resulting in their swelling. The migration of monomers into the galleries of nanolayers leads to the polymer formation between the intercalated sheets. The polymerization process can be initiated via different methods such as heat/radiation, diffusion of a suitable initiator such as organic ones, and catalysts fixed through cationic exchange inside the interlayer before the swelling of nanofillers. The polymerization of monomer between the interlayers will thereby form an intercalated or exfoliated nanocomposite (Karimi and Wan Daud, 2017) with a schematic illustration of the process shown in Fig. 3. The proper dispersion of nanofillers in the monomer solution before the polymerization process is a critical factor to guarantee the polymer formation between the NPs. Modifying the surface of the NPs by organic modifiers facilitates the better dispersion of NPs and the polymerization process. The in-situ intercalative polymerization is a proper fabricating method of both thermoplastics and thermoset polymers, and also the non-soluble and thermally stable PNCs. Some of the benefits of this method are cost-effectivity, high transparency, good dispersion of nanofillers, controllable particle morphology, and high interfacial adhesion of the nanofillers to the polymer matrix. Besides, it is possible to easily disperse higher content of nanofillers without any agglomeration compared to the case of melting methods in which the nanofiller dispersion is somewhat difficult due to the high viscosity of the solution. A high-performance nanocomposite will be then obtained due to the presence of a covalent bond among the NP functional groups and the polymer chains.

Implementation of Polymer Nanocomposites for Effluent Applications

Concerning the high importance of treating huge amount of industrial effluents that are annually released into the environment because of the rapid development of industrialization, different methods are available for the decontamination of the wastewater (Soetaredjo *et al.*, 2018; Rajasulochana and Preethy, 2016; Barakat, 2011), among which PNCs have attracted great attention because of their cost-effectivity, eco-friendly, and unique properties.

Polymer Nanocomposites as Adsorbents

Adsorption technique is one of the most commonly used techniques for the wastewater treatment. This technique is considered as a low-cost, simple, quick, and effective way of removing various kinds of organic and inorganic pollutants such as heavy metals (Ravikumar and Udayakumar, 2020; Zhang *et al.*, 2020), dyes (Yadav *et al.*, 2020), phenols (Hatami *et al.*, 2020; Bin-Dahman and Saleh, 2020), oil and grease (Lü *et al.*, 2016; Yu *et al.*, 2015), pharmaceuticals (Zhang *et al.*, 2016), and several other contaminants (Akhrame *et al.*, 2018). PNCs are considered as a high potential adsorbent for water and wastewater treatments as they possess extremely high surface area and associated sorption sites, short intraparticle diffusion distance, and tunable pore size and surface chemistry (Qu *et al.*, 2013).

Ptaszkowska-Koniarz *et al.* studied the adsorption of rhodamine B and sunset yellow FCF from the liquid phase onto resorcinol (Aldrich) and formaldehyde (Chempur) modified with methylamine and copper (II) chloride. They prepared the PNC based on the conventional sol-gel method. They found that the adsorption capacity towards rhodamine B and sunset yellow depended on some factors such as pH, temperature, and modification of materials using acid or bases. The adsorption capacity toward the removal of dyes increased by temperature increment of the process. The acidic medium helped the effective removal of the sunset yellow FCF, while the basic medium helped that of rhodamine B. They also proved that the modification of PNC increases the effective adsorption of dyes (Ptaszkowska-Koniarz *et al.*, 2017).

Horst *et al.* studied batch adsorption of heavy metal ions on magnetic/chitosan nanocomposites. The maximum adsorption capacity for removal of Zn, Cu, Cd, and Cr were respectively 72, 188, 159, and 46 (mg/g), which were considerably higher than those reported in the literature. The results also indicated that the adsorbents had satisfactory reusability with 5–8 reuse cycles. This allows their application in the removal of contaminants from water and wastewater (Horst *et al.*, 2016).

Lee *et al.* studied the removal of Cr(VI) ion from aqueous solution using polymer-based adsorbents. They used alginate/PVA-hematite nanocomposite which was prepared by entrapping a powdered form of hematite in alginate and PVA blend

hydrogels. The results showed that the maximum sorption capacity of the PNCs toward Cr(VI) was 12.501 mg/g. They found that Cr(VI) removal was highly sensitive to a pH between 2 and 9, and the highest removal capacity of adsorbents occurred at the highest acidic solution pH, decreasing sharply with increasing pH (Lee *et al.*, 2013).

Shahzad *et al.* investigated the removal of heavy metals, such as Pb(II), Cu(II), and As(III) from aqueous solutions using (EDTA)-functionalized magnetic chitosan GO nanocomposites. They prepared (EDTA-MCS/GO) using a reduction precipitation method. Their results indicated that the nanocomposite had an excellent removal ability with a maximum adsorption capacity of 206.52, 207.26, and 42.75 mg/g over Pb(II), Cu(II), and As(III), respectively. It was also found that various operating parameters, such as pH, temperature, metal ion concentration, and contact time influenced the adsorption effectiveness (Shahzad *et al.*, 2017).

Arya and Philip studied the removal of pharmaceuticals from wastewater using PNCs. They prepared clay: chitosan: powdered activated carbon: magnetic NPs nanocomposite adsorbent for removal of atenolol, ciprofloxacin, and gemfibrozil from wastewater. They also investigated the influence of solution pH, NP loading amount, and the acid or base used for modification of nanocomposite on the adsorption process. Results showed the successful application of magnetic chitosan nanocomposites for the removal of atenolol, ciprofloxacin, and gemfibrozil from the wastewater with a maximum adsorption capacity of 15.6, 39.1, and 24.8 mg/g, respectively (Arya and Philip, 2016).

Polymer Nanocomposites as Membrane Filters

In recent years, the usage of nanocomposite membranes has attracted the attention of scientists for the treatment of water and wastewater since the existing membranes, mainly polymers in nature, are still restricted by several challenges, including the trade-off between permeability and selectivity and low resistance to biofouling. PNC membranes are used for the removal of micro-organisms, chemical compounds, heavy metals, and other pollutants from waste streams such as agro-food (Cassano *et al.*, 2018), textile (Van der Bruggen *et al.*, 2004), petroleum industries (Parsaie *et al.*, 2020) or drinking water streams (Mukhopadhyay *et al.*, 2020). The nanocomposite membranes can be designed for different purposes by tuning their structure and physiochemical properties, such as hydrophilicity, porosity, charge density, and thermal and mechanical stability, leading to unique physiochemical properties such as excellent chemical and mechanical stability, electrical conductivity, reinforcement capability, and antifouling properties.

Generally, nanocomposite membranes are either produced by dispersing NPs into a polymer matrix or coating onto the membrane surface (Ursino *et al.*, 2018). Nor *et al.* prepared a nanocomposite membrane consisting of Polyvinylidene Fluoride (PVDF) and electrospun titanium dioxide (TiO₂) nanofibers, (PVDF/e-TiO₂), by hot pressing the as-spun TiO₂ nanofibers onto the PVDF flat sheet membrane. The TiO₂ nanofibers acted as photocatalysts to decompose the organic pollutants in the wastewater and the PVDF membrane acted as a support. The plate containing the TiO₂-PVDF membrane was placed in a hydraulic press system and pressed under a pressure of 80 bars. The hot press technique was carried out by setting the operating temperatures at 60 °C, 100 °C, 160 °C, and 180 °C for about 30 min. It was shown that the nanocomposite membrane prepared at a hot-pressing temperature of 100 °C exhibited appropriate morphological structure and physical properties. PVDF/e-TiO₂-100 exhibited the highest photocatalytic activity in the degradation of bisphenol A (BPA) under UV irradiation compared to PVDF/e-TiO₂-160 and PVDF/e-TiO₂-180. Their results also indicated that the introduction of TiO₂ nanofibers in PVDF-based nanocomposite membrane via hot pressing plays an important role in enhancing the degradation and filtration of organic pollutants such as BPA (Nor *et al.*, 2016).

In another study, Qin *et al.* prepared a new nanocomposite forward osmosis membrane (FO) for the simultaneous removal of oil and salt from shale gas wastewater. The prepared nanocomposite FO membrane was composed of an oil-repelling and salt rejecting hydrogel selective layer on top of GO nanosheets infused polymeric support layer. It was shown that the hydrogel selective layer leads to superior anti-fouling capability under any oil-water emulsions. On the other hand, this new FO membrane demonstrated more than three times higher water flux and higher removal for oil and salts (>99.9% for oil and >99.7% for multivalent ions). Results indicated that this new FO membrane has the merit to find application in treating highly saline and oily wastewater (Qin *et al.*, 2015).

Amoli-Diva *et al.* reported the preparation and characterization of PSF nanocomposites in which silver, cobalt, and nickel NPs were incorporated into the PSF materials for ultra-purification of wastewater. To prepare the nanocomposite membrane, PSF was dissolved in N, N-dimethyl acetamide (DMAc) and its surface was modified by adding 10% of the cobalt NPs and the solution was sonicated until forming a uniform homogenous casting suspension. Their results showed that PSF/Ni in the aqueous medium had the highest diffusion coefficient, the smallest particle size, and the smallest pore size compared to other prepared PSF thin-film membranes. Moreover, their results indicated that the pore size distribution influences the hydrophobic nature of the membrane as well as the diffusion behavior at the membrane interface. They proved that the diffusion coefficient may be used as an indication of the hydrophilicity of the membrane for the aqueous systems. Overall, it was shown that the incorporation of Ni and Co NPs into the modified PSF materials leads to a reduction in membrane fouling behavior (Amoli-Diva *et al.*, 2020).

In another study, Rahimi *et al.* fabricated an antifouling nanocomposite membrane from goethite (α -FeOOH) and polyethersulfone. It was reported that not only the membrane possessed excellent antifouling properties in long-term exposure with protein solution but it also showed a good selectivity and high dye removal capacity for Direct Red 16 (99%) (Rahimi *et al.*, 2016).

Lü *et al.* synthesized a thermosensitive poly(N-isopropylacrylamide)-grafted magnetic NPs (MIO@SiO₂) PNC to demulsify the oily droplets present in wastewater. The membrane showed very good oil removal from the aqueous solution and also a great ability to be reused with over 90% transmittance after the 7th reuse cycle (Lü *et al.*, 2016).

In another work, Qiu and He presented a new and efficient strategy to modify the nanocomposite membrane and constructed a zwitterion-silver nanocomposite structure via second interfacial polymerization of zwitterion and in-situ synthesis of silver NPs (Ag NPs). Results showed that compared with existing data reported in the literature, the modified zwitterion-silver nanocomposite membrane showed outstanding antifouling property (> 96% antimicrobial efficiency), high water flux, and excellent selectivity, which highlights its potential for practical applications (Qu and He, 2018).

Polymer Nanocomposites as Photocatalyst

Photocatalytic or catalytic oxidation is a process that is used to remove trace contaminants and microbial pathogens from wastewater. The use of PNCs with high surface area per volume in the photocatalytic process for the removal of pollutants from the wastewater is one of the most appealing and highly investigated research areas due to its great potential and high efficiency using sunlight to remove the organic pollutants and harmful bacteria. The use of sunlight as an energy source is an ideal method as it is a safe, renewable, and clean method (Dong *et al.*, 2015).

To prepare the PNCs for photocatalytic purposes, several kinds of polymers such as hyperbranched polyester, polyamide, poly(vinylidene difluoride)-*co*-trifluoroethylene, polyethersulfone, polyetherimide, polypyrrole, and polyvinyl alcohol (Akhrame *et al.*, 2018) and several kinds of fillers (considered as photocatalyst) such as ZnO, RGO, SnO₂, CeO₂, and TiO₂ can be used. Among fillers, TiO₂ is the most widely studied photocatalyst because of its non-toxicity, cost-effectivity, high chemical and photochemical stability, and unique photocatalyst efficiency (Dong *et al.*, 2015).

Photocatalytic degradation of inorganic pollutants

Yu *et al.* prepared BiPO₄-PANI heterostructure by hydrothermal method and hybridization. Their experimental results showed that BiPO₄-PANI could degrade several typical pollutants such as heavy metal ions and organic dyes under visible light. Based on their observations, PANI/BiPO₄ had an excellent ability for degradation of Hg(II) (95.3%), Cr(VI) (97.7%), and MB dye (95.8%) under 300 W xenon lamp (Yu *et al.*, 2018).

In another work, Shirmardi *et al.* studied the effect of PANI as an organic semiconductor on the photocatalytic performance of ZnSe NPs. They prepared Pristine ZnSe NPs and ZnSe/PANI nanocomposites by a simple and cost-effective co-precipitation method in the ambient conditions. The results showed an enhancement in the photocatalytic performance of ZnSe/PANI nanocomposites compared to the pristine ZnSe NPs for the conversion of Cr(VI) to Cr(III) in the aqueous solution (Shirmardi *et al.*, 2018).

Photocatalytic degradation of organic pollutants

Shanmugam *et al.* synthesized graphene-TiO₂ nanocomposites with enhanced photocatalytic properties for the degradation of organic pollutants present in wastewater. The G-TiO₂ nanocomposites were synthesized by the one-pot in-situ microwave method which is a novel surfactant-free, environmentally friendly method. Experiments showed that the surface area of pure TiO₂ and G-TiO₂ nanocomposite were 20.11 m²/g and 173.76 m²/g, respectively. The photocatalytic activity of the nanocomposites increased greatly due to the increment in the surface area. The results indicated the highest degradation efficiency of 97% by UV light and 96% by visible light irradiation, revealing the G-TiO₂ nanocomposite as an effective catalyst for industrial wastewater treatment both in the UV light and visible light (Shanmugam *et al.*, 2016).

Similarly, Duarah and Karak developed a sustainable hyperbranched polyurethane (HPU) nanocomposite with reduced carbon dot-zinc oxide nanohybrid (RCD-ZnO) as a prospective solar energy-assisted heterogeneous photocatalyst for the degradation of dodecyl benzenesulfonate and commercial detergent upon exposure to sunlight. The RCD-ZnO was fabricated with a starch-based HPU by an in-situ polymerization process. The synthesized PNCs exhibited high degradation of dodecyl benzenesulfonate (96.7% in 110 min) and commercial detergent (94.8% in 150 min) (Duarah and Karak, 2019).

In another work, Kumar *et al.* fabricated a novel photocatalyst polyacrylamide/Ni_{0.02}Zn_{0.98}O (PAM/NZO) by the addition of NPs during polymerization of acrylamide in an aqueous medium using ammonium persulfate and N,N'-acrylamide. The PNC showed high removal efficiency of 99.17% and 96.55% for rhodamine B and malachite green, respectively. The prepared nanocomposite had also a high recycling efficiency (Kumar *et al.*, 2014).

Although TiO₂ is the most popular NP for the fabrication of photocatalysts PNCs in wastewater remediation, other inorganic NPs are also employed for this purpose. Zhao *et al.* synthesized a new type of magnetic photocatalyst graphene/Fe₃O₄/NiO (GNs/Fe₃O₄/NiO) nanocomposite for the removal of organic pollutants in wastewater. They found that the composite materials had a perfect photocatalytic performance to degrade p-nitrophenol and rhodamine B. Moreover, the nanocomposites can be recycled easily by an extra magnetic field after photocatalytic degradation of p-nitrophenol and rhodamine B in wastewater. Therefore, this allows the magnetic nanocomposites to find great potential applications in the photocatalytic field in the future (Zhao *et al.*, 2015).

Romero Saez *et al.* fabricated a PNC photocatalyst using TiO₂ immobilized into LDPE and HDPE (10, 20 wt%) to degrade MO in an aqueous medium under visible light irradiation. TiO₂ was synthesized by the sol-gel process and the polymers were incorporated by impregnation. TiO₂(90)/LDPE photocatalyst showed the best degradation efficiency among all experimented PNCs after 180 min of reaction, without a notorious reduction in the degradation efficiency after three consecutive uses (Romero Saez *et al.*, 2017).

Zarrin and Heshmatpour reported the synthesis of PNCs using $\text{TiO}_2/\text{Nb}_2\text{O}_5/\text{PANI}$ and $\text{TiO}_2/\text{Nb}_2\text{O}_5/\text{RGO}$ nanocomposites for photocatalytic degradation of organic pollutants via the hydrothermal method, accompanied by the in-situ chemical oxidative polymerization. Their results indicated that under visible light the $\text{TiO}_2/\text{Nb}_2\text{O}_5/\text{RGO}$ exhibited significantly higher photocatalytic activity in the degradation of organic dyes (MB and MO dyes) in comparison with $\text{TiO}_2/\text{Nb}_2\text{O}_5/\text{PANI}$, $\text{TiO}_2/\text{Nb}_2\text{O}_5$, and pure TiO_2 (Zarrin and Heshmatpour, 2018).

Photocatalytic disinfection of biological pollutants

Malesic-Eleftheriadou *et al.* synthesized a bio-based polyethylene terephthalate- TiO_2 (PET- TiO_2) photocatalyst to remove antibiotics such as isoniazid, metronidazole, sulfadiazine, sulfamethoxazole, trimethoprim, norfloxacin, moxifloxacin, and lincomycin from the aqueous media. In their study, PET was used and evaluated as a supporting polymer for aerioxide P25 TiO_2 immobilization. Different composites with different TiO_2 content were prepared (10%, 30%, and 47% TiO_2). Results indicated that the immobilization of TiO_2 NPs was successful in all cases and higher photocatalyst concentration resulted in higher photodegradation efficiencies. Finally, it was proved that PET-10%- TiO_2 was efficient in the degradation of the antibiotic mixture present in water and wastewater (Malesic-Eleftheriadou *et al.*, 2019).

Pathania *et al.* prepared PANI zirconium (IV) silicophosphate (PANI-ZSP) nanocomposite via the sol-gel method by mixing PANI gel into the inorganic precipitates of zirconium(IV) silicophosphate (ZSP). Their study revealed that PANI-ZSP nanocomposite had a degradation efficiency of 82% for photocatalysis of MB dye from water and it was successfully used as an antibacterial agent against *Escherichia coli* (*E. coli*) (Pathania *et al.*, 2014).

Yao *et al.* presented the improvement of TiO_2 thin film photocatalytic efficiency under visible light ($\lambda > 400$ nm) by doping a novel photosensitive dye (5, 10, 15, 20-tetraphenyl-21H, 23H-porphine nickel, TPPN), using the sol-gel method. The TiO_2/TPPN thin film had a good inhibition rate for photocatalytic degradation of phytopathogenic bacteria including *Enterobacter cloacae* SM1, *Erwinia carotovora* subsp. *carotovora* 3, and *E. carotovora* subsp. *carotovora* 7 under visible light. These results indicated that TiO_2/TPPN thin film has a potential for the direct application to the plant protection under visible light irradiation in water systems (Yao *et al.*, 2007).

Polymer Nanocomposites as Disinfectants and Microbial Control Agents

It is well recognized that traditional methods such as free chlorine (Cl_2), chlorine dioxide (ClO_2), ozone (O_3), UV, and UV/chlorine (UV/ Cl_2), which are used for the removal of disinfectants and microbial agents might have an adverse effect on the treated wastewater (Luo *et al.*, 2020). Hence, the incorporation of a novel water disinfection method to overcome the limitations encountered by other methods is essential. An alternative method to remove the microbial agents from wastewater is the use of PNCs with MMT, Ag, ZnO, TiO_2 , CNT, and Graphene nanofillers.

Maddigpu *et al.* reported the application of carbon nanoparticles (CNPs) and chitosan (CHIT) in the form of CHIT-CNP nanocomposite for the disinfection of wastewater. The nanocomposite was prepared by the solution casting method. The results indicated that CHIT-CNP nanocomposite had a highly efficient antimicrobial activity for *E. coli* under solar irradiation when used in a recirculating compound parabolic collector (CPC) reactor (Maddigpu *et al.*, 2018).

Mahlangu *et al.* fabricated a dual-purpose magnetic PNC from $\text{Fe}_3\text{O}_4@\text{PPy-MAA}$ via in situ oxidative polymerization of the pyrrole monomer in a thioglycolic acid (mercaptoacetic), acid solution (as a dopant), in the presence of iron oxide (Fe_3O_4). The maximum adsorption capacity of the prepared PNC for Ag^+ was determined to be 833.33 mg/g at room temperature. They showed that the adsorbed Ag^+ can be used for the disinfection of microorganisms such as *E. coli*. Finally, the prepared PNC has an excellent ability for the removal of Ag^+ ions from wastewater, subsequently, the Ag^+ loaded waste material can be used for the disinfection of pollutants (Mahlangu *et al.*, 2019).

Lovatel *et al.* prepared a hybrid PNC from silver nanoparticles (Ag NPs) anchored onto MMT and dispersed in sodium alginate (ALG) polymeric matrix. The hybrid MMT-ALG-Ag NPs were tested for antibacterial activity by the agar diffusion test using two microorganisms (*E. coli* and *S. aureus*). According to their results, a reduction of 98.5% of the total coliforms was observed, which shows a better performance compared to the UV radiation, as a common method for disinfection of industrial wastewater (Lovatel *et al.*, 2015).

Polymer Nanocomposites as Sensing and Monitoring Devices

The growing concern about the public health and the environment has led to the search for effective methods to determine and quantify pollutants in water and wastewater. Due to the extremely low concentrations, high complexity of water/wastewater matrices, and lack of fast pathogen detection, water and wastewater treatment has faced a challenge in sensing and monitoring contaminants. Thus, the development of an accurate and high-quality method of monitoring the contaminant concentration is currently crucial. Several types of research have been done regarding PNC-based electrochemical and photochemical devices for water testing, among which the use of PNCs possesses unique properties such as excellent electrochemical, optical, and magnetic properties that help to improve their sensitivity, rate of detection, and possible multiple detection abilities (Qu *et al.*, 2013). The PNC-based sensors are designed to be sensitive to the pH changes, possess an affinity to the organic or inorganic contaminants and be able to monitor pathogens (Akhrame *et al.*, 2018).

Conjugated conducting PANI was fabricated onto titania nanoparticles (PANI-TiO_2 NPs) using a microwave-accelerated reaction system to selectively detect 1,2-diaminobenzene (1,2-DAB) in a phosphate buffer phase. The synthesized PANI-TiO_2 NPs

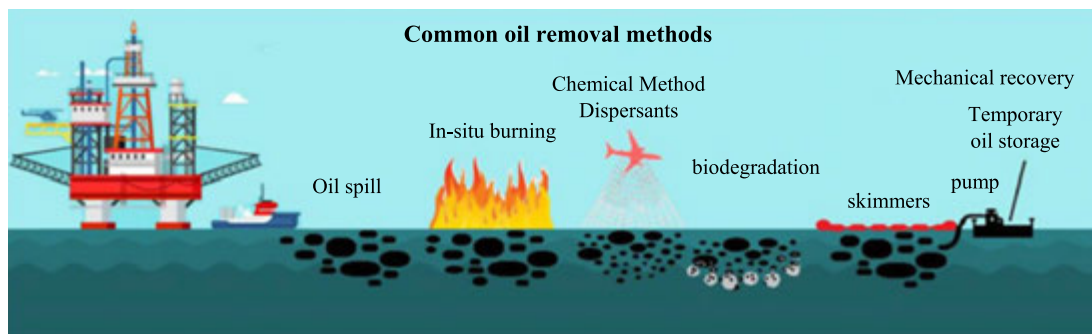


Fig. 4 Common methods used for removal of oil from oil-contaminated seawater. Reproduced from Gatou, M.-A., Lagopati, N., Tsoukleris, D., Pavlatou, E., 2020. Commercial sponges as a novel technology for crude oil removal from seawater and industrial wastewater: A review. *Biomedical Journal of Scientific & Technical Research* 25, 19426–19436.

were deposited on a glassy carbon electrode (GCE) as a thin film using Nafion as the conducting binder. The results indicated that the assembled (1,2-DAB) sensor was able to detect 1,2-DAB in real water samples with high accuracy in a short response time (12 s) (Karim *et al.*, 2020).

Tovide *et al.* fabricated a graphene PANI/tungsten oxide (PANI/WO₃/GR) nanocomposite sensor for the detection of phenanthrene in wastewater. The PNC was synthesized using electropolymerization of a mixture of aniline monomer and tungsten oxide on a graphene-modified glassy carbon electrode (GCE). The assembled sensor showed high phenanthrene detection sensitivity with a dynamic linear range of 1.0–6.0 pM and a detection limit of 0.123 pM which is more than three orders of magnitude lower than the WHO permissible level of 0.2 g/L for polyaromatic hydrocarbons in wastewater. The results also indicated that the sensor exhibited good reproducibility, long-term storage stability, and excellent sensitivity (Tovide *et al.*, 2014).

Devi and Umadevi synthesized a silver–PVA nanocomposite by a chemical reduction method in aqueous media for the detection of heavy metals in wastewater. Their results indicated that the PVA nanocomposite was able to detect the concentration of cadmium in water based on a linear change in surface plasmon resonance absorption strength. On the other hand, the PNC showed good antimicrobial activity against pathogenic bacteria, *E. coli*, and *Pseudomonas aeruginosa* (gram-negative), *Bacillus cereus*, and *Staphylococcus aureus* (gram-positive), which are commonly found in water (Devi and Umadevi, 2014).

In another study, Gutiérrez-Capitán *et al.* fabricated several electrochemical sensors for the rapid analysis of chemical oxygen demand (COD) in urban wastewaters by incorporating CNT-polystyrene composite and different inorganic nanofillers, such as Ni, NiCu alloy, CoO, and CuO/AgO. By comparing the response of the prepared sensors, the CuO/AgO-based nanocomposite sensor showed the best analytical performance for online detection of wastewater COD (Gutiérrez-Capitán *et al.*, 2015).

Other Applications of Polymer Nanocomposites for Wastewater Treatment

In a study conducted by Gatou *et al.* different methods of oil removal from the seawater or oil-contaminated effluents were discussed (Fig. 4). They claimed that commercial sponges such as melamine and polyurethane have attracted great attention in the field of crude oil removal both from seawater and industrial wastewater because of their low cost, low density, excellent mechanical properties, remarkable reusability, and high porous three-dimensional structure. However, the amphipathic nature of the commercial sponges usually limits their application for oil absorption and some modifications should be done to make the surface wettability towards the superhydrophobic/Superoleophilic state (Gatou *et al.*, 2020).

Parsaie *et al.* investigated the oil separation from the oil-contaminated seawater by a modified polyurethane sponge to remove the organic materials and oil from the oil/water systems. A robust superhydrophobic/superoleophilic polyurethane sponge comprising magnesium stearate NPs coating and the phenol-formaldehyde resin was developed by the cost-effective immersion method. The results showed that the optimum contact angle and sliding angle occurred at 175° and 3°, respectively. Regarding the small value of contact angle, the organic absorption time was less than 1 s, covering a wide absorption capacity range of 29–38 g/g depending on the viscosity and density of oils. They proved that the modified polyurethane sponge provided an excellent performance capability of the continuous oil/water separation, required for an industrial application (Parsaie *et al.*, 2020).

Conclusion

Polymer nanocomposites have gained the attention of scientists for water and wastewater treatment applications since they are cost-effective and eco-friendly. In this article, the types of PNCs which are applicable in industrial effluents were first described. Then a detailed explanation was given concerning with their fabrication methods including melting-based methods, solvent-based methods, and in-situ methods, and their industrial applications especially in water and wastewater treatment such as membranes,

adsorbents, photocatalysts, disinfectants, and sensors for monitoring contaminants and removal of all kinds of wastewater contaminants. Although many of the applications for the treatment of industrial effluents highlighted in this article are still in the laboratory stage, some of them have found their way to commercialization such as nanoadsorbents and photocatalysts. However, before the commercialization stage, the uncovered aspects such as the issues of toxicity, recyclability, and recovery should be also considered.

References

- Ahamad, T., Naushad, M., Mousa, R.H., Alshehri, S.M., 2020. Fabrication of starch-salicylaldehyde based polymer nanocomposite (pnc) for the removal of pollutants from contaminated water. *International Journal of Biological Macromolecules* 165, 2731–2738.
- Ahmad, S., Khan, S.B., Asiri, A.M., Marwani, H.M., Kamal, T., 2020. Polypeptide and copper oxide nanocomposite hydrogel for toxicity elimination of wastewater. *Journal of Sol-Gel Science and Technology* 96, 382–394.
- Ahmad, T., Danish, M., 2018. Prospects of banana waste utilization in wastewater treatment: A review. *Journal of Environmental Management* 206, 330–348.
- Ahmed, M.J., 2017. Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solution using activated carbons. *Environmental Toxicology and Pharmacology* 50, 1–10.
- Aigbe, U.O., Ho, W.H., Maity, A., Khenfouch, M., Srinivasu, V., 2018. Removal of hexavalent chromium from wastewater using ppy/Fe₃O₄ magnetic nanocomposite influenced by rotating magnetic field from two pole three-phase induction motor. *Journal of Physics: Conference Series* 984, 012008.
- Akhrame, M.O., Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I., Oputu, O.U., 2018. Polymeric nanocomposites (PNCs) for wastewater remediation: An overview. *Polymer-Plastics Technology and Engineering* 57, 1801–1827.
- Amini, M., Etemadi, H., Akbarzadeh, A., Yegani, R., 2017. Preparation and performance evaluation of high-density polyethylene/silica nanocomposite membranes in membrane bioreactor system. *Biochemical Engineering Journal* 127, 196–205.
- Amoli-Diva, M., Irani, E., Pourghazi, K., 2020. Photocatalytic filtration reactors equipped with bi-plasmonic nanocomposite/poly acrylic acid-modified polyamide membranes for industrial wastewater treatment. *Separation and Purification Technology* 236, 116257.
- Anastopoulos, I., Kyzas, G.Z., 2014. Agricultural peels for dye adsorption: A review of recent literature. *Journal of Molecular Liquids* 200, 381–389.
- Anastopoulos, I., Karamesouti, M., Mitropoulos, A.C., Kyzas, G.Z., 2017. A review for coffee adsorbents. *Journal of Molecular Liquids* 229, 555–565.
- Arya, V., Philip, L., 2016. Adsorption of pharmaceuticals in water using Fe₃O₄ coated polymer clay composite. *Microporous and Mesoporous Materials* 232, 273–280.
- Awasthi, A., Jadhao, P., Kumari, K., 2019. Clay nano-adsorbent: Structures, applications and mechanism for water treatment. *SN Applied Sciences* 1, 1076.
- Azeez, A.A., Rhee, K.Y., Park, S.J., Hui, D., 2013. Epoxy clay nanocomposites – Processing, properties and applications: A review. *Composites Part B: Engineering* 45, 308–320.
- Azizi, A., 2020. Green synthesized Fe₃O₄/cellulose nanocomposite suitable adsorbent for metronidazole removal. *Polymer Science, Series B* 62, 572–582.
- Badruddoza, A.Z.M., Shawon, Z.B.Z., Tay, W.J.D., Hidajat, K., Uddin, M.S., 2013. Fe₃O₄/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater. *Carbohydrate Polymers* 91, 322–332.
- Barakat, M., 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry* 4, 361–377.
- Basheer, B.V., George, J.J., Siengchin, S., Parameswaranpillai, J.S., 2020. Polymer grafted carbon nanotubes—Synthesis, properties, and applications: A review. *Nano-Structures & Nano-Objects* 22, 100429.
- Bassiyouni, M., Mansi, A., Elgabry, A., et al., 2020. Utilization of carbon nanotubes in removal of heavy metals from wastewater: A review of the cnts' potential and current challenges. *Applied Physics A* 126, 38.
- Bera, M., Maji, P., 2017. Graphene-based polymer nanocomposites: Materials for future revolution. *Polymer Science* 1, 00013.
- Betiha, M.A., Moustafa, Y.M., Mansour, A.S., Rafik, E., El-Shahat, M.F., 2020. Nontoxic polyvinylpyrrolidone-propylmethacrylate-silica nanocomposite for efficient adsorption of lead, copper, and nickel cations from contaminated wastewater. *Journal of Molecular Liquids* 314, 113656.
- Bhatnagar, A., Sillanpää, M., 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – A review. *Chemical Engineering Journal* 157, 277–296.
- Bhatnagar, A., Sillanpää, M., Witek-Krowiak, A., 2015. Agricultural waste peels as versatile biomass for water purification – A review. *Chemical Engineering Journal* 270, 244–271.
- Bhattacharya, M., 2016. Polymer nanocomposites – A comparison between carbon nanotubes, graphene, and clay as nanofillers. *Materials* 9, 262.
- Bhattacharyya, K.G., Gupta, S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science* 140, 114–131.
- Bin-Dahman, O.A., Saleh, T.A., 2020. Synthesis of carbon nanotubes grafted with peg and its efficiency for the removal of phenol from industrial wastewater. *Environmental Nanotechnology, Monitoring & Management* 13, 100286.
- Bosso, S., Enzweiler, J., 2002. Evaluation of heavy metal removal from aqueous solution onto scolecite. *Water Research* 36, 4795–4800.
- Cassano, A., Conidi, C., Ruby-Figueroa, R., Castro-Muñoz, R., 2018. Nanofiltration and tight ultrafiltration membranes for the recovery of polyphenols from agro-food by-products. *International Journal of Molecular Science* 19, 351.
- Davis, R.D., Gilman, J.W., VanderHart, D.L., 2003. Processing degradation of polyamide 6/montmorillonite clay nanocomposites and clay organic modifier. *Polymer Degradation and Stability* 79, 111–121.
- de Oliveira, A.D., Beatrice, C.A.G., 2018. Polymer nanocomposites with different types of nanofiller. In: Sivasankaran, S. (Ed.), *Nanocomposites-Recent Evolutions*. IntechOpen, pp. 103–104.
- Devi, J.M., Umadevi, M., 2014. Synthesis and characterization of silver-pva nanocomposite for sensor and antibacterial applications. *Journal of Cluster Science* 25, 639–650.
- Dong, Q., Ding, Y., Wen, B., et al., 2012. Improvement of thermal stability of polypropylene using dopo-immobilized silica nanoparticles. *Colloid and Polymer Science* 290, 1371–1380.
- Dong, S., Feng, J., Fan, M., et al., 2015. Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: A review. *RSC Advances* 5, 14610–14630.
- Duarah, R., Karak, N., 2019. Hyperbranched polyurethane/reduced carbon dot-zinc oxide nanocomposite-mediated solar-assisted photocatalytic degradation of organic contaminant: An approach towards environmental remediation. *Chemical Engineering Journal* 370, 716–728.
- Esmat, M., Farghali, A.A., Khedr, M.H., El-Sherbiny, I.M., 2017. Alginate-based nanocomposites for efficient removal of heavy metal ions. *International Journal of Biological Macromolecules* 102, 272–283.
- Fan, Q., Li, Z., Zhao, H., et al., 2009. Adsorption of Pb (II) on palygorskite from aqueous solution: Effects of pH, ionic strength and temperature. *Applied Clay Science* 45, 111–116.
- Feng, L., Xie, N., Zhong, J., 2014. Carbon nanofibers and their composites: A review of synthesizing, properties and applications. *Materials* 7, 3919–3945.
- Fischer, H., 2003. Polymer nanocomposites: From fundamental research to specific applications. *Materials Science and Engineering: C* 23, 763–772.
- Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management* 92, 407–418.

- Gandhi, M.R., Viswanathan, N., Meenakshi, S., 2010. Adsorption mechanism of hexavalent chromium removal using amberlite ira 743 resin. *Ion Exchange Letters* 3, 25–35.
- Gatou, M.-A., Lagopati, N., Tsoukleris, D., Pavlatou, E., 2020. Commercial sponges as a novel technology for crude oil removal from seawater and industrial wastewater: A review. *Biomedical Journal of Scientific & Technical Research* 25, 19426–19436.
- Goyal, R.K., 2017. *Nanomaterials and Nanocomposites: Synthesis, properties, characterization techniques, and Applications*. CRC Press.
- Gu, J., Xiao, P., Chen, J., *et al.*, 2014. Janus polymer/carbon nanotube hybrid membranes for oil/water separation. *ACS Applied Materials & Interfaces* 6, 16204–16209.
- Guo, F., Aryana, S., Han, Y., Jiao, Y., 2018. A review of the synthesis and applications of polymer–nanoclay composites. *Journal of Applied Sciences* 8, 1696.
- Gupta, V.K., Pathania, D., Agarwal, S., Singh, P., 2012. Adsorptional photocatalytic degradation of methylene blue onto pectin–cus nanocomposite under solar light. *Journal of Hazardous Materials* 243, 179–186.
- Gupta, V.K., Pathania, D., Kothiyal, N.C., Sharma, G., 2014. Polyaniline zirconium (iv) silicophosphate nanocomposite for remediation of methylene blue dye from waste water. *Journal of Molecular Liquids* 190, 139–145.
- Gurses, A., 2015. *Introduction to Polymer-Clay Nanocomposites*. CRC Press.
- Gutiérrez-Capitán, M., Baldi, A., Gómez, R., *et al.*, 2015. Electrochemical nanocomposite-derived sensor for the analysis of chemical oxygen demand in urban wastewaters. *Analytical Chemistry* 87, 2152–2160.
- Han, H., Rafiq, M.K., Zhou, T., *et al.*, 2019. A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. *Journal of Hazardous Materials* 369, 780–796.
- Hatami, M., Panah, M.Y., Mahmoudian, M., 2020. Facile production of HNTs_PDA_PF nanocomposites by unique and environment-friendly method for the removal of phenolic pollutants in water as an environmental adsorbent. *Journal of the Taiwan Institute of Chemical Engineers* 108, 1–15.
- Horst, M.F., Alvarez, M., Lassalle, V.L., 2016. Removal of heavy metals from wastewater using magnetic nanocomposites: Analysis of the experimental conditions. *Separation Science and Technology* 51, 550–563.
- Hou, C., Jiao, T., Xing, R., *et al.*, 2017. Preparation of TiO₂ nanoparticles modified electrospun nanocomposite membranes toward efficient dye degradation for wastewater treatment. *Journal of the Taiwan Institute of Chemical Engineers* 78, 118–126.
- Huskić, M., Žigon, M., Ivanković, M., 2013. Comparison of the properties of clay polymer nanocomposites prepared by montmorillonite modified by silane and by quaternary ammonium salts. *Applied Clay Science* 85, 109–115.
- Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature* 354, 56–58.
- Inglezakis, V.J., Loizidou, M.D., Grigoropoulou, H.P., 2003. Ion exchange of Pb²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ on natural clinoptilolite: Selectivity determination and influence of acidity on metal uptake. *Journal of Colloid and Interface Science* 261, 49–54.
- Isawi, H., 2020. Using zeolite/polyvinyl alcohol/sodium alginate nanocomposite beads for removal of some heavy metals from wastewater. *Arabian Journal of Chemistry* 13, 5691–5716.
- Jannapu Reddy, R., 2010. *Preparation, Characterization and Properties of Injection Molded Graphene Nanocomposites*. Wichita State University.
- Kango, S., Kalia, S., Celli, A., *et al.*, 2013. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites – A review. *Progress in Polymer Science* 38, 1232–1261.
- Karim, M.R., Alam, M.M., Aijaz, M.O., *et al.*, 2020. The fabrication of a chemical sensor with pani-TiO₂ nanocomposites. *RSC Advances* 10, 12224–12233.
- Karimi, A., Wan Daud, W.M.A., 2017. Materials, preparation, and characterization of pva/mmt nanocomposite hydrogels: A review. *Polymer Composites* 38, 1086–1102.
- Khajepour, M., Gelves, G.A., Sundararaj, U., 2015. Modification of montmorillonite with alkyl silanes and fluorosurfactant for clay/fluoroelastomer (FKM) nanocomposites. *Clays and Clay Minerals* 63, 1–14.
- Khalid, A., Abdel-Karim, A., Ali Atieh, M., Javed, S., McKay, G., 2018. Peg-cnts nanocomposite PSU membranes for wastewater treatment by membrane bioreactor. *Separation and Purification Technology* 190, 165–176.
- Khan, W.S., Hamadneh, N.N., Khan, W.A., 2016. Polymer nanocomposites – Synthesis techniques, classification and properties. In: Sia, P.D. (Ed.), *Science and Applications of Tailored Nanostructures*. One Central Press, p. 50.
- Khare, R., Bose, S., 2005. Carbon nanotube based composites – A review. *Journal of Minerals and Materials Characterization and Engineering* 4, 31–46.
- Koo, J.H., 2006. *Polymer Nanocomposites*. McGraw-Hill Professional Pub.
- Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F., Smalley, R.E., 1985. C₆₀: Buckminsterfullerene. *Nature* 318, 162–163.
- Kumar, A., Sharma, G., Naushad, M., Singh, P., Kalia, S., 2014. Polyacrylamide/Ni_{0.02}Zn_{0.98}O nanocomposite with high solar light photocatalytic activity and efficient adsorption capacity for toxic dye removal. *Industrial & Engineering Chemistry Research* 53, 15549–15560.
- Kumar, S.K., Jouault, N., Benicewicz, B., Neely, T., 2013. Nanocomposites with polymer grafted nanoparticles. *Macromolecules* 46, 3199–3214.
- Kumararaja, P., Manjiaiah, K., Datta, S., Shabeer, T.A., Sarkar, B., 2018. Chitosan-g-poly (acrylic acid)-bentonite composite: A potential immobilizing agent of heavy metals in soil. *Cellulose* 25, 3985–3999.
- Lee, I., Lee, C.G., Park, J.A., *et al.*, 2013. Removal of Cr(VI) from aqueous solution using alginate/polyvinyl alcohol–hematite composite. *Desalination and Water Treatment* 51, 3438–3444.
- Lee, S.M., Tiwari, D., 2012. Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. *Applied Clay Science* 59–60, 84–102.
- Lovatel, R.H., Neves, R.M., Oliveira, G.R., *et al.*, 2015. Disinfection of biologically treated industrial wastewater using montmorillonite/alginate/nanosilver hybrids. *Journal of Water Process Engineering* 7, 273–279.
- Lü, T., Zhang, S., Qi, D., Zhang, D., Zhao, H., 2016. Thermosensitive poly(*n*-isopropylacrylamide)-grafted magnetic nanoparticles for efficient treatment of emulsified oily wastewater. *Journal of Alloys and Compounds* 688, 513–520.
- Luo, Y., Feng, L., Liu, Y., Zhang, L., 2020. Disinfection by-products formation and acute toxicity variation of hospital wastewater under different disinfection processes. *Separation and Purification Technology* 238, 116405.
- Maddipati, P.R., Sawant, B., Wanjari, S., *et al.*, 2018. Carbon nanoparticles for solar disinfection of water. *Journal of Hazardous Materials* 343, 157–165.
- Mahdavinia, G.R., Soleymani, M., Sabzi, M., Azimi, H., Atlasi, Z., 2017. Novel magnetic polyvinyl alcohol/laponite RD nanocomposite hydrogels for efficient removal of methylene blue. *Journal of Environmental Chemical Engineering* 5, 2617–2630.
- Mahlangu, T., Das, R., Abia, L.K., *et al.*, 2019. Thiol-modified magnetic polypyrrole nanocomposite: An effective adsorbent for the adsorption of silver ions from aqueous solution and subsequent water disinfection by silver-laden nanocomposite. *Chemical Engineering Journal* 360, 423–434.
- Malesic-Eleftheriadou, N., Evgenidou, E., Kyzas, G.Z., Bikiaris, D.N., Lambropoulou, D.A., 2019. Removal of antibiotics in aqueous media by using new synthesized bio-based poly(ethylene terephthalate)-TiO₂ photocatalysts. *Chemosphere* 234, 746–755.
- Mallakpour, S., Marefatpour, F., 2014. Novel chiral poly (amide-imide)/surface modified SiO₂ nanocomposites based on *n*-trimellitylimido-L-methionine: Synthesis and a morphological study. *Progress in Organic Coatings* 77, 1271–1276.
- Mallakpour, S., Naghdi, M., 2018. Polymer/SiO₂ nanocomposites: Production and applications. *Progress in Materials Science* 97, 409–447.
- Mansor, M.R., Akop, M.Z., 2020. 9 - polymer nanocomposites smart materials for energy applications. In: Bouhfid, R., Qaiss, A.E.K., Jawaid, M. (Eds.), *Polymer Nanocomposite-based Smart Materials*. Woodhead Publishing, pp. 157–176.
- Miranda-Trevino, J.C., Coles, C.A., 2003. Kaolinite properties, structure and influence of metal retention on ph. *Applied Clay Science* 23, 133–139.
- Mirmohseni, A., Dorraji, M.S., Figoli, A., Tasselli, F., 2012. Chitosan hollow fibers as effective biosorbent toward dye: Preparation and modeling. *Bioresource Technology* 121, 212–220.
- Mistretta, M., Morreale, M., La Mantia, F., 2014. Thermomechanical degradation of polyethylene/polyamide 6 blend-clay nanocomposites. *Polymer Degradation and Stability* 99, 61–67.

- Mohan, D., Sarswat, A., Ok, Y.S., Pittman Jr, C.U., 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresource Technology* 160, 191–202.
- Mukhopadhyay, R., Bhaduri, D., Sarkar, B., *et al.*, 2020. Clay–polymer nanocomposites: Progress and challenges for use in sustainable water treatment. *Journal of Hazardous Materials* 383, 121125.
- Mukhopadhyay, R., Manjaiah, K., Datta, S., Yadav, R., Sarkar, B., 2017. Inorganically modified clay minerals: Preparation, characterization, and arsenic adsorption in contaminated water and soil. *Applied Clay Science* 147, 1–10.
- Nasrollahzadeh, M., Sajjadi, M., Iravani, S., Varma, R.S., 2021. Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano)materials for sustainable water treatment: A review. *Carbohydrate Polymers* 251, 116986.
- Naz, A., Kausar, A., Siddiq, M., Choudhary, M.A., 2016. Comparative review on structure, properties, fabrication techniques, and relevance of polymer nanocomposites reinforced with carbon nanotube and graphite fillers. *Polymer-Plastics Technology and Engineering* 55, 171–198.
- Nerkar, N.V., Kondawar, S.B., Brahme, S.K., Kim, Y.H., 2018. Polyaniline/ZnO nanocomposites for the removal of methyl orange dye from waste water. *International Journal of Modern Physics B* 32, 1840085.
- Nethaji, S., Sivasamy, A., Mandal, A., 2013. Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr (vi). *Bioresource Technology* 134, 94–100.
- Nor, N.A.M., Jaafar, J., Ismail, A.F., *et al.*, 2016. Preparation and performance of pvdf-based nanocomposite membrane consisting of TiO₂ nanofibers for organic pollutant decomposition in wastewater under UV irradiation. *Desalination* 391, 89–97.
- Olu-Owolabi, B.I., Alabi, A.H., Diagboya, P.N., Unuabonah, E.I., Düring, R.-A., 2017. Adsorptive removal of 2, 4, 6-trichlorophenol in aqueous solution using calcined kaolinite-biomass composites. *Journal of Environmental Management* 192, 94–99.
- Pai, S., Kini, M.S., Selvaraj, R., 2021. A review on adsorptive removal of dyes from wastewater by hydroxyapatite nanocomposites. *Environmental Science and Pollution Research* 28, 11835–11849.
- Palansooriya, K.N., Yang, Y., Tsang, Y.F., *et al.*, 2020. Occurrence of contaminants in drinking water sources and the potential of biochar for water quality improvement: A review. *Critical Reviews in Environmental Science and Technology* 50, 549–611.
- Parsaie, A., Mohammadi-Khanaposhtani, M., Riazi, M., Tamsilian, Y., 2020. Magnesium stearate-coated superhydrophobic sponge for oil/water separation: Synthesis, properties, application. *Separation and Purification Technology* 251, 117105.
- Passador, F., Ruvoilo-Filho, A., Pessan, L., 2017. Nanocomposites of polymer matrices and lamellar clays. *Nanostructures*, 187–207.
- Pathania, D., Katwal, R., Sharma, G., *et al.*, 2016. Novel guar gum/Al₂O₃ nanocomposite as an effective photocatalyst for the degradation of malachite green dye. *International Journal of Biological Macromolecules* 87, 366–374.
- Pathania, D., Sharma, G., Kumar, A., Kothiyal, N.C., 2014. Fabrication of nanocomposite polyaniline zirconium(iv) silicophosphate for photocatalytic and antimicrobial activity. *Journal of Alloys and Compounds* 588, 668–675.
- Patra, A.S., Ghorai, S., Sarkar, D., *et al.*, 2017. Anionically functionalized guar gum embedded with silica nanoparticles: An efficient nanocomposite adsorbent for rapid adsorptive removal of toxic cationic dyes and metal ions. *Bioresource Technology* 225, 367–376.
- Pavlidou, S., Papaspyrides, C., 2008. A review on polymer-layered silicate nanocomposites. *Progress in Polymer Science* 33, 1119–1198.
- Perez, J.J., Villanueva, M.E., Sánchez, L., *et al.*, 2020. Low cost and regenerable composites based on chitin/bentonite for the adsorption potential emerging pollutants. *Applied Clay Science* 194, 105703.
- Premarathna, K., Rajapaksha, A.U., Sarkar, B., *et al.*, 2019. Biochar-based engineered composites for sorptive decontamination of water: A review. *Chemical Engineering Journal* 372, 536–550.
- Ptaszkowska-Koniarz, M., Goscianska, J., Pietrzak, R., 2017. Adsorption of dyes on the surface of polymer nanocomposites modified with methylamine and copper(II) chloride. *Journal of Colloid and Interface Science* 504, 549–560.
- Qin, D., Liu, Z., Sun, D.D., *et al.*, 2015. A new nanocomposite forward osmosis membrane custom-designed for treating shale gas wastewater. *Scientific Reports* 5, 14530.
- Qiu, M., He, C., 2018. Novel zwitterion-silver nanocomposite modified thin-film composite forward osmosis membrane with simultaneous improved water flux and biofouling resistance property. *Applied Surface Science* 455, 492–501.
- Qu, X., Alvarez, P.J.J., Li, Q., 2013. Applications of nanotechnology in water and wastewater treatment. *Water Research* 47, 3931–3946.
- Rafiee, M.A., Rafiee, J., Wang, Z., *et al.*, 2009. Enhanced mechanical properties of nanocomposites at low graphene content. *ACS Nano* 3, 3884–3890.
- Rafiee, H.R., Shirvani, M., Ogunseitan, O.A., 2016. Removal of lead from aqueous solutions by a poly(acrylic acid)/bentonite nanocomposite. *Applied Water Science* 6, 331–338.
- Rahimi, M., Zinadini, S., Zinatizadeh, A.A., *et al.*, 2016. Hydrophilic goethite nanoparticle as a novel antifouling agent in fabrication of nanocomposite polyethersulfone membrane. *Journal of Applied Polymer Science* 133.
- Rahmandoust, M., Ayatollahi, M.R., 2016. Carbon nanotubes. In: *Characterization of carbon nanotube based composites under consideration of defects*. Springer, pp. 5–63.
- Rajapaksha, A.U., Dilrukshi Premarathna, K.S., Gunarathne, V., Ahmed, A., Vithanage, M., 2019. Chapter 9 – Sorptive removal of pharmaceutical and personal care products from water and wastewater. In: Prasad, M.N.V., Vithanage, M., Kapley, A. (Eds.), *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*. Butterworth-Heinemann, pp. 213–238.
- Rajasulochana, P., Preethy, V., 2016. Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review. *Resource-Efficient Technologies* 2, 175–184.
- Rane, A.V., Kanny, K., Abitha, V., Thomas, S., 2018. Methods for synthesis of nanoparticles and fabrication of nanocomposites. In: Bhagyaraj, S.M., Oluwafemi, O.S., Kalarikkal, N., Thomas, S. (Eds.), *Synthesis of Inorganic Nanomaterials*. Elsevier, pp. 121–139.
- Rani, M., Rachna, Shanker, U., 2020. Metal oxide-chitosan based nanocomposites for efficient degradation of carcinogenic PAHs. *Journal of Environmental Chemical Engineering* 8, 103810.
- Raval, N.P., Shah, P.U., Shah, N.K., 2016. Adsorptive removal of nickel (ii) ions from aqueous environment: A review. *Journal of Environmental Management* 179, 1–20.
- Ravikumar, K., Udayakumar, J., 2020. Preparation and characterisation of green clay-polymer nanocomposite for heavy metals removal. *Chemistry and Ecology* 36, 270–291.
- Ray, S.S., Okamoto, M., 2003. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer Science* 28, 1539–1641.
- Rivas, B.L., Munoz, C., 2009. Synthesis and metal ion adsorption properties of poly (4–sodium styrene sulfonate-co-acrylic acid). *Journal of Applied Polymer Science* 114, 1587–1592.
- Rodríguez, C., Leiva, E., 2020. Enhanced heavy metal removal from acid mine drainage wastewater using double-oxidized multiwalled carbon nanotubes. *Molecules* 25, 111.
- Romero Saez, M., Jaramillo, L., Saravanan, R., *et al.*, 2017. Notable photocatalytic activity of TiO₂-polyethylene nanocomposites for visible light degradation of organic pollutants. *EXPRESS Polymer Letters* 11, 899–909.
- Romero-Sáez, M., Jaramillo, L., R, S., *et al.*, 2017. Notable photocatalytic activity of TiO₂-polyethylene nanocomposites for visible light degradation of organic pollutants. *Express Polymer Letters* 11, 899–909.
- Rusmin, R., Sarkar, B., Liu, Y., McClure, S., Naidu, R., 2015. Structural evolution of chitosan–palygorskite composites and removal of aqueous lead by composite beads. *Applied Surface Science* 353, 363–375.
- Saeedi-Jurkueyeh, A., Jafari, A.J., Kalantary, R.R., Esrafil, A., 2020. A novel synthetic thin-film nanocomposite forward osmosis membrane modified by graphene oxide and polyethylene glycol for heavy metals removal from aqueous solutions. *Reactive and Functional Polymers* 146, 104397.
- Safdari, M., Al-Haik, M., 2013. Synergistic electrical and thermal transport properties of hybrid polymeric nanocomposites based on carbon nanotubes and graphite nanoplatelets. *Carbon* 64, 111–121.

- Sarkar, B., Rusmin, R., Ugochukwu, U.C., Mukhopadhyay, R., Manjiaiah, K.M., 2019. Modified clay minerals for environmental applications. In: Mercurio, M., Sarkar, B., Langella, A. (Eds.), *Modified Clay and Zeolite Nanocomposite Materials*. Elsevier, pp. 113–127.
- Sengodu, P., Deshmukh, A.D., 2015. Conducting polymers and their inorganic composites for advanced Li-ion batteries: A review. *RSC Advances* 5, 42109–42130.
- Shabaan, O.A., Jahin, H.S., Mohamed, G.G., 2020. Removal of anionic and cationic dyes from wastewater by adsorption using multiwall carbon nanotubes. *Arabian Journal of Chemistry* 13, 4797–4810.
- Shaheen, S.M., Niazi, N.K., Hassan, N.E., *et al.*, 2019. Wood-based biochar for the removal of potentially toxic elements in water and wastewater: A critical review. *International Materials Reviews* 64, 216–247.
- Shahzad, A., Miran, W., Rasool, K., *et al.*, 2017. Heavy metals removal by EDTA-functionalized chitosan graphene oxide nanocomposites. *RSC Advances* 7, 9764–9771.
- Shakoor, M.B., Niazi, N.K., Bibi, I., *et al.*, 2018. Arsenic removal by natural and chemically modified water melon rind in aqueous solutions and groundwater. *Science of the Total Environment* 645, 1444–1455.
- Shanmugam, M., Alsalmi, A., Alghamdi, A., Jayavel, R., 2016. In-situ microwave synthesis of graphene-TiO₂ nanocomposites with enhanced photocatalytic properties for the degradation of organic pollutants. *Journal of Photochemistry and Photobiology B: Biology* 163, 216–223.
- Shawky, H.A., Chae, S.-R., Lin, S., Wiesner, M.R., 2011. Synthesis and characterization of a carbon nanotube/polymer nanocomposite membrane for water treatment. *Desalination* 272, 46–50.
- Sheikh, M., Pazirofteh, M., Dehghani, M., *et al.*, 2020. Application of ZnO nanostructures in ceramic and polymeric membranes for water and wastewater technologies: A review. *Chemical Engineering Journal* 391, 123475.
- Shi, C., Zhang, L., Bian, H., *et al.*, 2020. Construction of Ag-ZnO/cellulose nanocomposites via tunable cellulose size for improving photocatalytic performance. *Journal of Cleaner Production*, 125089.
- Shirmardi, A., Teridi, M.A.M., Azimi, H.R., *et al.*, 2018. Enhanced photocatalytic performance of ZnSe/PANI nanocomposites for degradation of organic and inorganic pollutants. *Applied Surface Science* 462, 730–738.
- Shirsath, S.R., Patil, A.P., Patil, R., *et al.*, 2013. Removal of brilliant green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study. *Ultrasonics Sonochemistry* 20, 914–923.
- Shokri, E., Shahed, E., Hermani, M., Etemadi, H., 2020. Towards enhanced fouling resistance of PVC ultrafiltration membrane using modified montmorillonite with folic acid. *Applied Clay Science* 200, 105906.
- Shrivastava, A., 2018. Chapter 1 – Introduction to plastics engineering. In: Shrivastava, A. (Ed.), *Introduction to Plastics Engineering*. William Andrew Publishing, pp. 1–16.
- Singh, N., Nagpal, G., Agrawal, S., 2018. Water purification by using adsorbents: A review. *Environmental Technology & Innovation* 11, 187–240.
- Soetaredjo, F.E., Ismadi, S., Foe, K., Yi-Hsu, J., 2018. Chapter 21 – Recent advances in the application of polymer-based nanocomposites for removal of hazardous substances from water and wastewater. In: Hussain, C.M., Mishra, A.K. (Eds.), *New Polymer Nanocomposites for Environmental Remediation*. Elsevier, pp. 499–540.
- Sun, X.-F., Liu, B., Jing, Z., Wang, H., 2015. Preparation and adsorption property of xylan/poly(acrylic acid) magnetic nanocomposite hydrogel adsorbent. *Carbohydrate Polymers* 118, 16–23.
- Syafalni, S., Sing, S., Zawawi, M., 2014. Sorption of dye wastewater by using natural zeolite, anionic-cationic surfactant modified zeolite and cationic surfactant modified zeolite. *World Applied Sciences Journal* 32, 818–824.
- Szczepanik, B., 2017. Photocatalytic degradation of organic contaminants over clay-TiO₂ nanocomposites: A review. *Applied Clay Science* 141, 227–239.
- Tanahashi, M., 2010. Development of fabrication methods of filler/polymer nanocomposites: With focus on simple melt-compounding-based approach without surface modification of nanofillers. *Materials* 3, 1593–1619.
- Tovide, O., Jaheed, N., Mohamed, N., *et al.*, 2014. Graphenated polyaniline-doped tungsten oxide nanocomposite sensor for real time determination of phenanthrene. *Electrochimica Acta* 128, 138–148.
- Unuabonah, E.I., Taubert, A., 2014. Clay-polymer nanocomposites (CPNs): Adsorbents of the future for water treatment. *Applied Clay Science* 99, 83–92.
- Unuabonah, E.I., Ugwuja, C.G., Omorogie, M.O., Adewuyi, A., Oladoja, N.A., 2018. Clays for efficient disinfection of bacteria in water. *Applied Clay Science* 151, 211–223.
- Ursino, C., Castro-Muñoz, R., Drioli, E., *et al.*, 2018. Progress of nanocomposite membranes for water treatment. *Membranes* 8, 18.
- Van der Bruggen, B., Curcio, E., Drioli, E., 2004. Process intensification in the textile industry: The role of membrane technology. *Journal of Environmental Management* 73, 267–274.
- Vellaichamy, B., Periakaruppan, P., Nagulan, B., 2017. Reduction of Cr⁶⁺ from wastewater using a novel in situ-synthesized pani/MnO₂/TiO₂ nanocomposite: Renewable, selective, stable, and synergistic catalysis. *ACS Sustainable Chemistry & Engineering* 5, 9313–9324.
- Xie, T., Reddy, K.R., Wang, C., Yargicoglu, E., Spokas, K., 2015. Characteristics and applications of biochar for environmental remediation: A review. *Critical Reviews in Environmental Science and Technology* 45, 939–969.
- Yadav, S., Asthana, A., Chakraborty, R., *et al.*, 2020. Cationic dye removal using novel magnetic/activated charcoal/ β -cyclodextrin/alginate polymer nanocomposite. *Nanomaterials* 10, 170.
- Yadav, V.B., Gadi, R., Kalra, S., 2019. Clay based nanocomposites for removal of heavy metals from water: A review. *Journal of Environmental Management* 232, 803–817.
- Yan, H., Yang, H., Li, A., Cheng, R., 2016. pH-tunable surface charge of chitosan/graphene oxide composite adsorbent for efficient removal of multiple pollutants from water. *Chemical Engineering Journal* 284, 1397–1405.
- Yao, K.S., Wang, D.Y., Chang, C.Y., *et al.*, 2007. Photocatalytic disinfection of phytopathogenic bacteria by dye-sensitized TiO₂ thin film activated by visible light. *Surface and Coatings Technology* 202, 1329–1332.
- Yu, L., Hao, G., Gu, J., *et al.*, 2015. Fe₃O₄/PS magnetic nanoparticles: Synthesis, characterization and their application as sorbents of oil from waste water. *Journal of Magnetism and Magnetic Materials* 394, 14–21.
- Yu, W.J., Cheng, Y., Zou, T., *et al.*, 2018. Preparation of BiPO₄-polyaniline hybrid and its enhanced photocatalytic performance. *Nano* 13, 1850009.
- Zahrán, M., Marei, A.H., 2019. Innovative natural polymer metal nanocomposites and their antimicrobial activity. *International Journal of Biological Macromolecules* 136, 586–596.
- Zarrin, S., Heshmatpour, F., 2018. Photocatalytic activity of TiO₂/Nb₂O₅/PANI and TiO₂/Nb₂O₅/RGO as new nanocomposites for degradation of organic pollutants. *Journal of Hazardous Materials* 351, 147–159.
- Zhang, M., Zhang, Z., Peng, Y., *et al.*, 2020. Novel cationic polymer modified magnetic chitosan beads for efficient adsorption of heavy metals and dyes over a wide pH range. *International Journal of Biological Macromolecules* 156, 289–301.
- Zhang, S., Dong, Y., Yang, Z., *et al.*, 2016. Adsorption of pharmaceuticals on chitosan-based magnetic composite particles with core-brush topology. *Chemical Engineering Journal* 304, 325–334.
- Zhao, D., Qiu, Q., Wang, Y., *et al.*, 2016. Efficient removal of acid dye from aqueous solutions via adsorption using low-cost blast-furnace slag. *Desalination and Water Treatment* 57, 28486–28495.
- Zhao, G., Mo, Z., Zhang, P., *et al.*, 2015. Synthesis of graphene/Fe₃O₄/NiO magnetic nanocomposites and its application in photocatalytic degradation the organic pollutants in wastewater. *Journal of Porous Materials* 22, 1245–1253.
- Zhu, R., Chen, Q., Zhou, Q., *et al.*, 2016. Adsorbents based on montmorillonite for contaminant removal from water: A review. *Applied Clay Science* 123, 239–258.
- Zhuang, S., Zhu, X., Wang, J., 2020. Adsorptive removal of plasticizer (dimethyl phthalate) and antibiotic (sulfamethazine) from municipal wastewater by magnetic carbon nanotubes. *Journal of Molecular Liquid* 319, 114267.

Additive Manufacturing of Polymer Matrix Composites

Farnoosh Pahlevanzadeh, Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran

Hamid Reza Bakhsheshi-Rad, Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran and Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Dermot Brabazon, I-Form, Advanced Manufacturing Research Centre, and Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Dublin, Ireland

Mahshid Kharaziha, Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran

Ahmad Fauzi Ismail, Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Safian Sharif, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia

Mahmood Razzaghi, Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

Filippo Berto, Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway

© 2021 Elsevier Inc. All rights reserved.

Introduction

The process of adding material layer by layer for fabricating parts from their 3D models (CAD data) is called AM, against the conventional subtractive fabricating processes. The other names for the AM method are 3D printing, RP, and SFF (Parandoush and Lin, 2017). The 3D printing process as a concept was presented in the 1970s with the development of inkjet printing, but the printing of materials instead of ink was introduced in the 1980s with inventing a process called SLA (Horvath, 2014). The SLA process, which Charles Hull invented, allowed manufacturers to fabricate the parts to save production time, money, and energy (de Leon *et al.*, 2016). Fabrication of the 3D components with complicated geometries and high accuracy is essential for AM methods (Vaezi *et al.*, 2013). Besides, the AM methods can be more cost-effective compared to the conventional manufacturing processes (Ngo *et al.*, 2018). Many innovative AM methods have been developed in recent decades, using numerous raw materials for different industries such as biomedical, automotive, aerospace, architectural design, and digital art (Parandoush and Lin, 2017). The most common materials used in the 3D printing industry are polymers because of their low cost, low melting point, low weight, process flexibility, diversity, and ease of adoption to different 3D printing methods (Ngo *et al.*, 2018; Wang *et al.*, 2017). However, 3D printed parts composed of monolithic polymers typically can only be used as conceptual prototypes because of their inferior mechanical properties.

The researches have aimed to resolve the low strength of the 3D printed polymers, which led to the development of numerous methods and materials for manufacturing advanced polymeric composites with improved strength (Wang *et al.*, 2017; Takezawa and Kobashi, 2017). Therefore, the fabrication of polymer matrix composites (PMCs), with superior mechanical performance and proper functionality could be possible by enhancing polymers with particle, fiber, or nanomaterial reinforcements (Wang *et al.*, 2017). PMCs are very attractive materials because of their available simple fabrication processes and low cost. Using monolithic polymers as structural materials are imperfect due to their inferior mechanical characteristics like low strength, elastic modulus, and impact resistance. One possible route for fabricating PMCs is reinforcing polymers by a network of strong fibers (Joseph *et al.*, 2012). The possibility of applying 3D printing of polymers and PMCs has been examined for many years in different industries like aerospace, automotive, biomedical, and electronics (Ngo *et al.*, 2018). Different selections of material types for 3D printing of PMCs has resulted in fabricating light-weight structures with complicated geometries in the aerospace industry (Horn and Harysson, 2012), reduction of material waste, time bottleneck, and setup costs in the electronics (Saengchairat *et al.*, 2017), and printing of organs and tissues in the biomedical industry (Javaid and Haleem, 2018a) (Wang *et al.*, 2017; Joseph *et al.*, 2012). In this article, different AM processes of PMCs, with a reinforced polymeric matrix to attain a fabricated part with superior strength and functionality, are reviewed. Besides, different reinforcing strategies of PMCs for using in 3D printing of customized and complicated geometries and the wide range of AM applications are discussed in detail.

Additive Manufacturing Methods Used for Fabricating PMCs

The available forms of polymers for applying in AM processes are powder, resin, filament, and reactive monomer, which are utilized for 3D printing of monolithic polymers and PMCs (Balla *et al.*, 2019). The most extensively studied AM processes for fabricating PMCs are SLA, SLS, FFF, DIW, and BJ, as shown in Fig. 1.

Stereolithography (SLA)

The SLA was the first marketed 3D printing method invented by Chuck Hull in 1986 (Pahlevanzadeh *et al.*, 2020a). An SLA system consists of a container that keeps photocurable liquid resin, a source of laser (typically UV light) that induces the polymerization

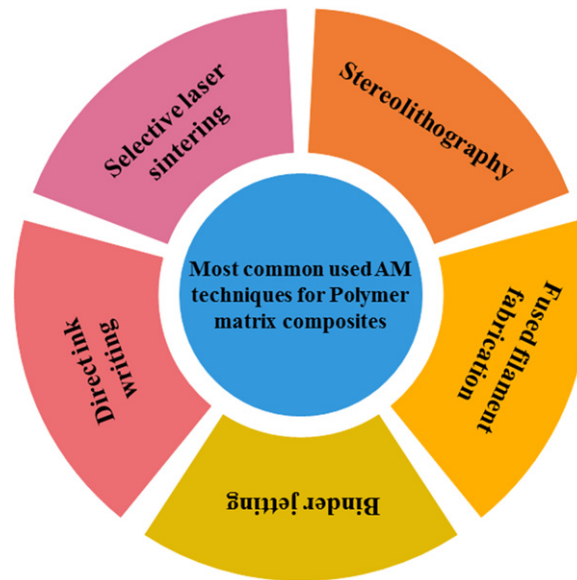


Fig. 1 The most extensively studied AM processes for fabricating PMCs.

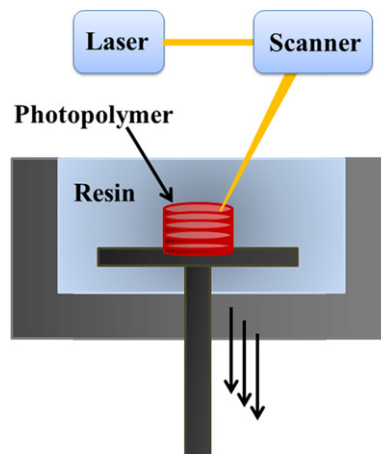


Fig. 2 Schematic illustration of SLA configuration. Reproduced from Li, J., Wu, C., Chu, P.K., Gelinsky, M., 2020. 3D printing of hydrogels: Rational design strategies and emerging biomedical applications. *Materials Science and Engineering: R: Reports* 140, 100543.

and cross-linking of liquid resin, a system that allows the horizontal plane (X and Y directions) movement of the laser beam, and a system that controls the vertical plane (z-direction) movement of fabrication platform. The main parts of a SLA system and their configuration to allow for the layer-by-layer AM process is depicted schematically in [Fig. 2](#); ([Li et al., 2020](#)). Irradiation of UV light to the liquid resin surface in a two-dimensional pattern solidifies it through absorbing a single photon to a predefined depth that is usually higher than the step height of the manufacturing platform. Because of that, uncured functional groups on the primary layer after photopolymerization will be polymerized during irradiation for curing the subsequent layer of liquid resin ([Manapat et al., 2017](#)). The manufacturing of the platform goes forward in the Z-direction upon curing layer by layer of resin for creating the solidified 3D construct with a possible resolution of 30 μm ([Mondschein et al., 2017](#)). For promoting mechanical properties, post-processes of curing the manufactured 3D construct with UV light and residual resin washing-off are usually needed because of the possible incomplete reaction of functional groups ([Li et al., 2020](#)).

Selective Laser Sintering (SLS)

The SLS is an AM process that can be used for fabricating complex 3D components by sintering layer by layer of powder material. Sintering of the powder particles is obtained by fusing selected areas of the powder layers made by supplied thermal energy via a laser beam, as illustrated in [Fig. 3](#). A beam deflection system, which can be a Galvano mirror, makes the scanning of the beam on selected areas of each layer based on the corresponding cross-section of the component as extracted from its CAD data. A thin layer

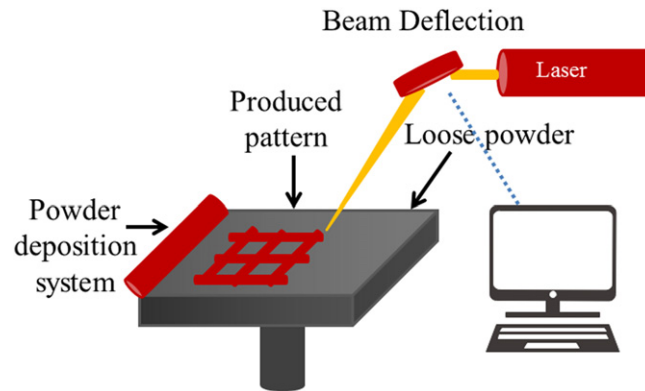


Fig. 3 Schematic overview of the SLS process.

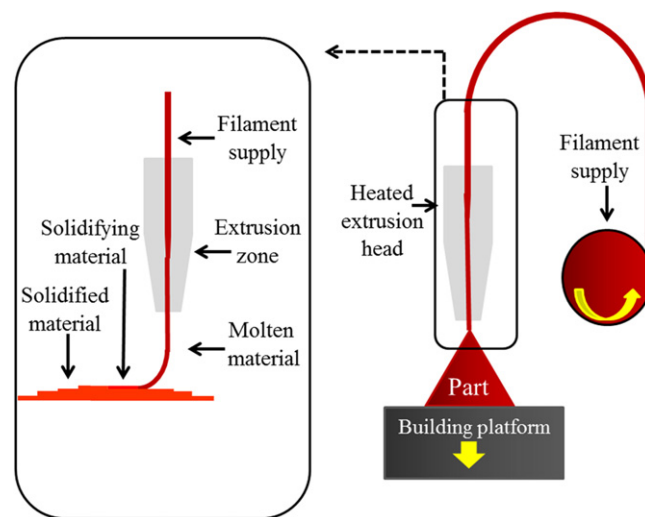


Fig. 4 Schematic illustration of the FFF process. Reproduced from Singh, S., Singh, G., Prakash, C., Ramakrishna, S., 2020. Current status and future directions of fused filament fabrication. *Journal of Manufacturing Processes* 55, 288–306.

of powder, typically with a thickness of 0.1–0.3 mm, is deposited in the building container by a powder deposition system before the laser sintering of that layer (Kruth *et al.*, 2003). As the SLS is a solvent-free process, it has an advantage that offers faster production as compared to the AM processes that need a solvent that requires the printed part to be left for evaporating the solvent (Fina *et al.*, 2017). The polymeric powder materials were the first and are still the most used materials for the SLS process (Kruth *et al.*, 2003). Both amorphous polymers (e.g., polycarbonate) and semi-crystalline polymers (e.g., nylons) have been utilized in the SLS method. Besides, the PMCs could be 3D printed by the SLS process (Kruth *et al.*, 2003).

Fused Filament Fabrication (FFF)

The FFF is one of the most used 3D printing processes with the maximum number of applications in all 3D printing sectors (Singh *et al.*, 2020). Some advantages, such as high flexibilities in the 3D printing process and high cost-effectiveness, have gained the largest share for the FFF process in the 3D printing industry since 2011 (Singh *et al.*, 2020; Brenken *et al.*, 2018). As depicted in Fig. 4 (Singh *et al.*, 2020) schematically, the 3D printers applying FFF technology typically have a thermoplastic filament unrolled from a roll such that the material is pushed toward one or more extrusion nozzles. The material is heated up to its semi-molten condition in the nozzle for preparing the creation of successive layers. The extrusion head can drive both horizontal and vertical paths applying a numerical control mechanism and using a software (Pranzo *et al.*, 2018). The FFF 3D printing process has many other advantages, including the availability of a wide range of nontoxic materials, easily changeable, low machine and maintenance costs, low temperature operating process, and compact 3D printers. Nevertheless, the main disadvantages of the FFF method are imperfect sticking of the material between layers and tool paths, roughness in finishing surface, the requirement of support material in 3D printing, and its removal after 3D printing, and long-time needed for creating the parts with big size (Au *et al.*, 2016).

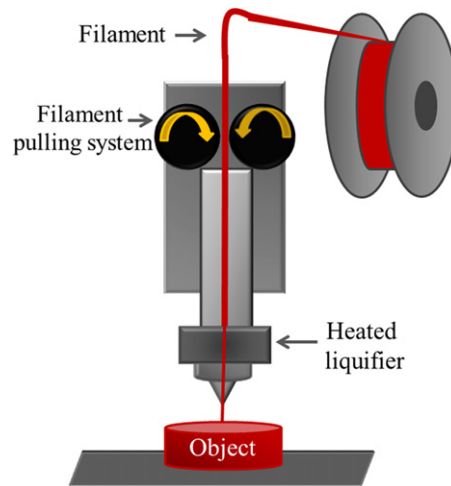


Fig. 5 Schematic illustration of the FDM process. Reproduced from Carneiro, O.S., Silva, A.F., Gomes, R., 2015. Fused deposition modeling with polypropylene. *Materials & Design* 83, 768–776.

Fused Deposition Modeling (FDM)

The FDM is an AM process, in which a molten thermoplastic material is deposited horizontally, extruded from a nozzle head, manufacturing the part with successive layers. The two most common materials applied in the FDM process are ABS and PLA (Carneiro *et al.*, 2015). Fig. 5 illustrates the FDM process schematically (Carneiro *et al.*, 2015) in order to better understand this method. In this process, a filament is melted at a temperature above its melting point inside the liquefier head and is pushed through the nozzle die by the pressure of still solid upstream filament. With moving the head, the extruded molten polymer is laid down, and the layer is shaped, starting with its perimeters and subsequently filling the inside of the layer (Too *et al.*, 2002). The advantages of the FDM process are high reliability of the process, relatively low initial investment materials cost. The FDM printers could be operated in office environments, with short manufacturing time for the components with thin walls. The process has low material waste that is limited to the supporting structures (Carneiro *et al.*, 2015). The other drawback of the FDM process is that the applied materials in this process have a low melting point, and if the printing objects need support on the overhangs, they will have a rough surface finish, requiring a time-consuming hand-working process for improving surface appearance (Carneiro *et al.*, 2015).

Direct Ink Writing (DIW)

The DIW is a 3D printing process in which a viscous ink as its raw material is extruded from a syringe, applying pneumatic pressure. In this extrusion-based process, different polymers like epoxy and photocurable acrylic resin mixed with reinforcements like silicon carbide whiskers, nylon fibers, and carbon fibers could be printed. The DIW is a user-friendly technology that has been employed efficiently in the biomedical industry for tissue engineering applications (Guvendiren *et al.*, 2016). In the DIW process, the 3D object is printed through the horizontal and vertical movement of the syringe. Fig. 6 shows the process of DIW schematically (Guvendiren *et al.*, 2016), which in this method, at the first step, resin and its curing agent are mixed before loading into the syringe as ink. After extrusion of the ink, it is cured by applying UV induction or thermal heating (Bekas *et al.*, 2019; Lebel *et al.*, 2010). The DIW methods can be divided into two categories of droplet-based approaches and filamentary-based approaches (Seerden *et al.*, 2001; Lewis, 2006). Different designs of ink, including polymer melts, highly shear-thinning colloidal suspensions, waxes, and concentrated polyelectrolyte complexes, have been employed for the DIW process. The method of solidification of mentioned inks could be either through temperature, liquid evaporation, gelation, or solvent-induced phase change (Lewis, 2006).

Binder Jetting (BJ)

The BJ process was developed in the early 1990s at the Massachusetts Institute of Technology (MIT) (Sachs *et al.*, 1990). Fig. 7 depicts a typical process of the BJ technique (Brunello *et al.*, 2016), for the printing of each layer of the object, a layer of powder is spread typically using a counter-rotating roller. Then, the liquid binding agent jets to the powder bed by an inkjet print-head to create the layer's two-dimensional pattern. Heating may be used for helping of curing and moisture control for some binder/powder systems, but it is not a basic requirement for the process (Ziaee and Crane, 2019). After printing each layer, the built platform is lowered to make room for printing the next layer, and the process is repeated. The objects just after 3D printing by the BJ technique are fragile and typically need post processes for improving the mechanical properties (Ziaee and Crane, 2019; Gaytan *et al.*, 2015; Qu, 2020). The key to success in the BJ process is selecting an efficient binder. The binder must be printable and preferably have low viscosity. The low viscosity of the binder allows forming the stream of individual droplet beads and

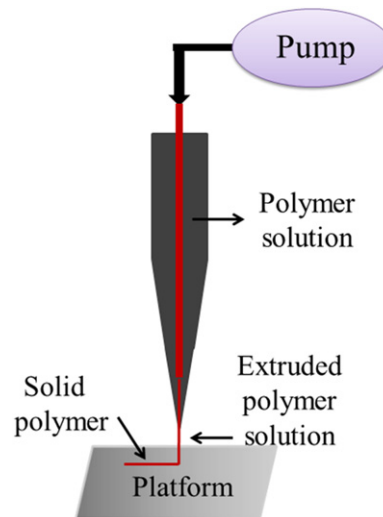


Fig. 6 Illustration of DIW process. Reproduced from Guvendiren, M., Molde, J., Soares, R.M., Kohn, J., 2016. Designing biomaterials for 3D printing. *ACS Biomaterials Science & Engineering* 2 (10), 1679–1693.

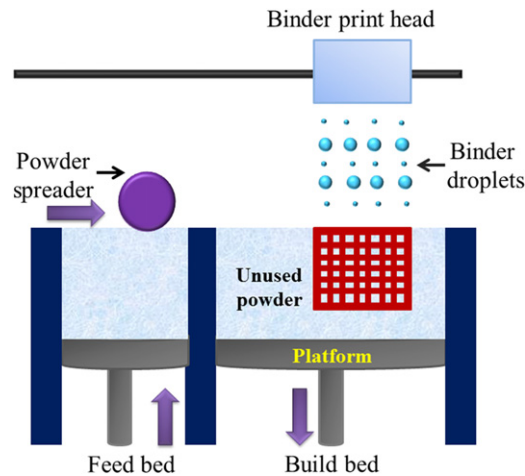


Fig. 7 Schematic illustration of BJ process. Reproduced from Brunello, G., Sivoletta, S., Meneghello, R., *et al.*, 2016. Powder-based 3D printing for bone tissue engineering. *Biotechnology Advances* 34 (5), 740–753.

subsequently rapidly breaking off from the nozzles (Ziaee and Crane, 2019). The primary particle bonding techniques generally are categorized as In-Liquid and In-Bed binding. In the In-Liquid binding, the binder is completely carried by jetted liquid while in the In-Bed binding; a rheologically simple liquid is printed and interacts with dry glue particles embedded in the powder bed. The interparticle bonds are initiated upon hydration (Utela *et al.*, 2008). The In-Liquid solutions cause more premature failure of print-head than the In-Bed mechanism because of the drying of the glue agent in the nozzles but offer a wider range of power systems (De Gans *et al.*, 2004). Commonly used In-Liquid binders that contain organic cross-linking agent (Ziaee and Crane, 2019) are butyral resins (Ziaee and Crane, 2019), polyvinyl (Ziaee and Crane, 2019), polysiloxanes (Reis *et al.*, 2005), PAA (Moon *et al.*, 2002) and acrysol (Yoo *et al.*, 1993). They typically decompose thermally during post-processing and leave little residue. Photo-curing polymers can be used for reducing challenges in binder migration after printing (Ziaee and Crane, 2019).

Polymer Matrix Composites (Natural Based or Synthetic Based)

Polymeric materials in the liquid state or the low melting temperature are extensively applied in the 3D printing industry because of their light-weight, low cost, and high flexibility in the process. These 3D printed polymeric products suffer from inferior mechanical properties and functionality as a big challenge for their extensive applications (Wang *et al.*, 2017). The composite materials consist of two or more phases that are different in chemical and physical specifications and are separated by an interface. The composites have a matrix phase, and the other phase or phases are dispersed in the matrix, and the bulk properties of the

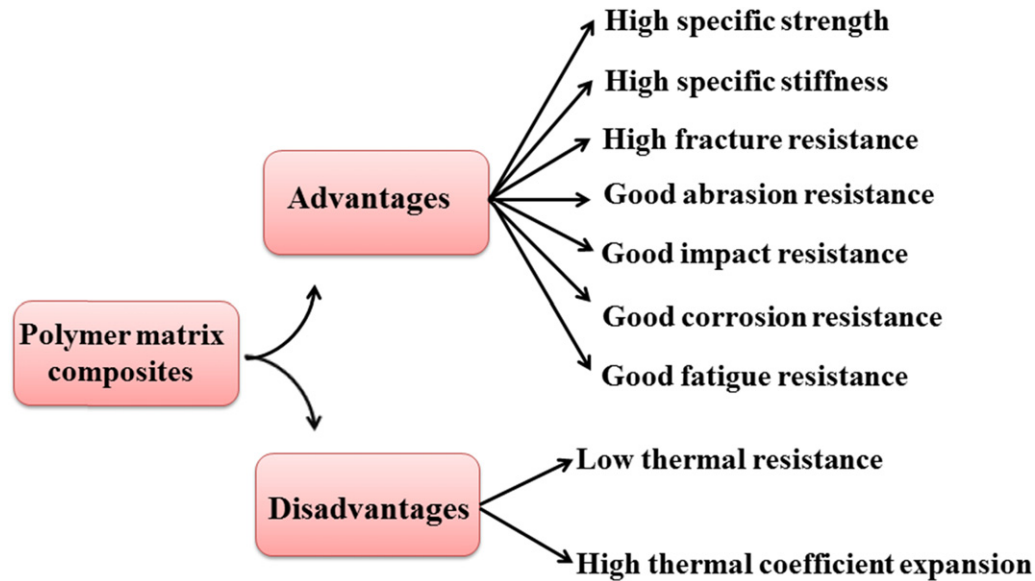


Fig. 8 Advantages and disadvantages of polymer matrix composites (PMCs).

composites are remarkably different from those of any of the composite ingredients (Joseph *et al.*, 2012). Based on the matrix type, which could be metal, ceramic, or polymer, the composites are categorized into MMCs, CMCs, and PMCs, respectively (Avila *et al.*, 2003 and Balla *et al.*, 2019) in this chapter, we have focused on the PMCs, which have many advantages against very few drawbacks as presented in Fig. 8. PMCs that are reinforced with different materials in the form of fibers (short and continuous) and particles (in the size of micro or nano) have been successfully manufactured by AM techniques, which will be described in detail in the following subsections.

3D Printing of the Fiber-Reinforced PMCs

The fiber reinforcements can remarkably improve the properties of polymeric matrix materials. Fibers-reinforced PMCs are vital materials with various applications because of their specifications, like high specific strength, acceptable corrosion behavior, and rigidity (Saroia *et al.*, 2020). The 3D printing processes commonly used for producing fiber-reinforced PMCs are FDM and DIW technologies (Wang *et al.*, 2017). The fiber-reinforced PMCs have different applications in the automotive, aerospace, and biomedical industries due to their high chemical resistance and good mechanical properties. Carbon fibers and glass fibers are commonly used for reinforcing the polymeric matrixes in the PMCs used in AM processes (Wu *et al.*, 2020; Ning *et al.*, 2015; De Mori *et al.*, 2018; Markstedt *et al.*, 2015). While the PMCs reinforced with short or chopped fibers are easier for processing, the PMCs reinforced with continuous fibers usually display comparatively superior tensile properties in the printing direction (De Mori *et al.*, 2018).

Table 1 represents the results of several pieces of research relating to the fiber-reinforced PMCs and their effects on the produced PMCs. For instance, Markstedt *et al.* (2015) improved the compressive modulus of alginate (75–250 kPa) by reinforcing it with cellulose nanofibers. Based on the results, the 3D printed scaffolds supported the cultured human chondrocytes, in which 73%–86% of viability was observed after one and seven days. The same bio-ink composition, consisting of cellulose nanofibers in the alginate matrix, combined with human chondrocytes and mesenchymal stromal cells, were found for promoting in vivo chondrogenesis after subcutaneous implantation of the 3D printed constructs in mice. The research results presented the potential capability of 3D bio-printing of human cartilage for the clinical applications (Apelgren *et al.*, 2017). In another research, Carneiro *et al.* (2015) used glass fiber reinforced PP composite for fabricating 3D printed parts applying the FDM process. Their investigations showed that the tensile strength and modulus enhanced by 40% and 30%, respectively, compared with the monolithic PP. Besides, they showed that 0° printing orientation has better mechanical properties compared to 45°, crossed 45° ($\pm 45^\circ$), and 90° printing orientations, in the same conditions (Carneiro *et al.*, 2015). The fibers orientation is one of the main parameters that influence the efficiency of fibers in the enhancement of the polymeric matrix. For investigating the effect of fibers orientation, Compton and Lewis. performed some experiments applying the DIW process (Compton and Lewis, 2014). For the preparation of the ink, they added both SiC whiskers and carbon fibers to the reinforced epoxy resin as a cellular matrix composite. These bio-inspired wood structures were fabricated with precise design parameters. In the 3D printed objects, high stiffness and toughness were seen as they maintained the orientation and alignment of fiber and whiskers (Compton and Lewis, 2014).

The other important parameter that influences the mechanical properties of 3D printed fiber-reinforced PMC is the fiber content. Ning *et al.* (2015) presented that the fiber content has a remarkable effect on the mechanical characteristics of carbon fiber

Table 1 Methods and materials applied for 3D printing of fiber-reinforced polymer matrix composites (PMCs)

Polymeric matrix	Reinforcement fiber	3D printing method	Results	References
Polypropylene	–	FDM	Production of objects with suitable mechanical performance	Carneiro <i>et al.</i> (2015)
Plastic materials	Carbon	FDM	Betterment of the mechanical properties	Ning <i>et al.</i> (2015)
Alginate	Nanocellulose	3D Bioprinting	Suitable support for living cells and help to cartilage tissue growth	Markstedt <i>et al.</i> (2015)
Alginate	Cellulose	3D Bioprinting	Good proliferation ability, cover of 17.2% of the surface areas with chondrocytes during 60 days.	Apelgren <i>et al.</i> (2017)
Epoxy resin, Nano-clay platelets	Carbon	Extrusion based printing	Appropriate mechanical properties with control on fibers orientation	Compton and Lewis (2014)
PLA	Carbon	FDM	Improvement of e tensile and flexural strengths	Li <i>et al.</i> (2016)
PLA	Carbon	FDM	Promising elastic modulus obtained from tensile results	Van Der Klift <i>et al.</i> (2016)
PLA	ZnO	Solvent cast 3D printing	Providing a promising product for medical and packaging applications	Nonato <i>et al.</i> (2019)
Nylon	Carbon	FDM	3D printing of continuous fiber-reinforced thermoplastics	Matsuzaki <i>et al.</i> (2016)
ABS	Carbon	FDM	Increased stiffness, tensile strength, and modulus	Shofner <i>et al.</i> (2003)
ABS	Glass	FDM	Improvement of the strength of an ABS filament	Zhong <i>et al.</i> (2001)
Thermoset resin	Carbon	DIW	Obtained complex geometries, a high order of fiber alignment within the microstructure of the composite	Lewicki <i>et al.</i> (2017)
Epoxy	Carbon	FDM	Betterment of mechanical performance of the 3D printed thermosetting composites	Hao <i>et al.</i> (2018)
PLA	Carbon	FDM	Significant enhancements of tensile and bending properties of PLA	Heidari-Rarani <i>et al.</i> (2019)

reinforced ABS composite 3D printed with FDM technology. The researchers showed that an increment of fiber content up to some limit would improve the mechanical properties of the printed composite, but further content of fiber would have a reverse influence on the properties because of the porosity increasing on the part. The outcomes revealed that with up to 5 wt% of fiber concentration, the best mechanical properties were obtained rather than higher content. As mentioned before, continuous fibers have a higher effect on the improvement of mechanical properties of PMCs compared to the short fibers as the continuous fibers can be oriented in the 3D printing direction. Regarding this issue, Li *et al.* evaluated continuous fiber-reinforced PLA composite, 3D printed by the FDM process (Li *et al.*, 2016). Their outcomes showed that the improvement in tensile and flexural strengths in continuous fiber-reinforced specimens was 13.8% and 164% higher than the short fibers reinforced PMCs, respectively (Li *et al.*, 2016). Nevertheless, 3D printing of continuous fiber-reinforced PMCs is challenging, and researchers are trying to develop an appropriate and standard paradigm for it (Saroia *et al.*, 2020).

3D Printing of Particle Reinforced PMCs

The particle reinforcements have been widely used to enhance the properties of the polymeric matrixes because of their low cost. Particles can be easily mixed with polymers, in all forms of powder, for use in the SLS process, liquid for use in the SLA process, and also could be extruded into printable filaments for use in FDM (Wang *et al.*, 2017). Commercialization and real-world applications of the polymers are addressed and resolved with the development of PMCs. Lately, Hwang *et al.* (2015) utilized the FDM process to investigate the thermo-mechanical properties of metal reinforced PMCs. They used copper and iron particles with an average size of fewer than 24 and 43 μm , respectively. The metallic particulate reinforcements with different concentrations from 10% to 80% were used for observing the influences on the properties of the 3D printed composite. Raising the temperature during extrusion from 190°C to 220°C increased the tensile strength while the viscosity was reduced. Besides, the ductility was increased with raising the reinforcement content but commenced to decline when the filler content exceeded a particular amount (Chung, 2001).

The existence of the particulate reinforcements in the polymeric matrix can improve the physical, chemical, and mechanical properties of the matrix. Besides, the presence of reinforcement particles can solve some difficulties encountered during the printing process. One of the key issues of the printing process is loose bonding between the layers because of high thermal expansion in monolithic polymers. The incorporation of metallic particles can decrease the thermal expansion of the resulted composite and helps for the better bonding of the layers (Chung, 2001).

3D printing of cell-laden scaffolds applying various hydrogel compositions (e.g., alginate, chitosan, and gelatin), reinforced with HAP particles, have been investigated (Kesti *et al.*, 2015; Wenz *et al.*, 2017). The results have been shown that the addition of

HAp particles can remarkably improve the mechanical characteristics of the hydrogels and promote osteogenic differentiation *in vivo*, making them appropriate for repairing bone tissue defects (Wenz *et al.*, 2017; Bendtsen *et al.*, 2017).

Nikzad *et al.* (2011) studied the influence of reinforcing the ABS matrix with copper and iron particles. The outcomes showed that the presence of the iron particles decreased the tensile strength of ABS and the resulted composite was harder and more brittle than the matrix. Masood and Song *et al.* developed a metallic powder reinforce PMC by incorporating iron particles in different sizes ranging from less than 30 to 80 μm in the P301 nylon matrix (Masood and Song, 2004). The resulted composite was found appropriate for direct rapid tooling applications. It was also found that the reinforcements with larger particle sizes can decline the mechanical properties of the 3D printed object. In other words, it revealed that the particulate reinforcements with smaller particle sizes could better enhance the properties of the polymeric matrix. In the next subsections, the usage of nanomaterials for the improvement of PMCs properties will be discussed.

3D Printing of PMCs Reinforced by Nanomaterials

Recent advances in nanoscience and nanotechnology have facilitated the development of nanocomposites with excellent mechanical and thermal properties at a remarkably lower weight. A composite is called nanocomposite when one of the reinforcement dimensions would be less than 100 nm (Francis and Jain, 2015). The polymer-based nanocomposites could be processed the same way as pure polymers without considering the machine for use in AM. Different types of polymer-based nanocomposites using different nanosized reinforcements have been developed for AM applications (Wu *et al.*, 2020). Nanomaterials like CNTs (Yan *et al.*, 2016; Pahlevanzadeh *et al.*, 2019b), graphene (Gray *et al.*, 1998), graphite (Sengupta *et al.*, 2011), ceramic (Pahlevanzadeh *et al.*, 2019a, 2018) and metallic nanoparticles (Zhang *et al.*, 2006) have exhibited excellent mechanical, electrical and thermal properties. Thus, the incorporation of nanomaterials into polymers for 3D printing could allow the fabrication of high-performance functional nanocomposites. Nanomaterials have been applied for enhancing the mechanical characteristics of 3D printed polymer-based components (Wang *et al.*, 2017). In addition, for improving the mechanical properties of PMCs, graphene-based materials can influence the cellular behavior of composites and induce cell proliferation and stem cell differentiation. Some nanomaterials added to polymers for the fabrication of appropriate PMCs for use in AM processes and their effect on the resulting nanocomposites are listed in Table 2. For example, Huang *et al.* (2017) investigated the incorporation of low concentration (up to 25 ppm) of graphene nanomaterials to the PU matrix. The results showed that the addition of nanosized graphene has significantly enhanced the oxygen metabolism and neural differentiation of NSCs. Besides, the samples containing 25 ppm graphene exhibited higher gene expression results than those in 10 ppm graphene reinforced (Huang *et al.*, 2017). In another research, Wei *et al.* (2015) tried to improve the electrical conductance of ABS material by incorporation of nanosized graphene applying the FDM process. The results showed that by incorporating 5.6 wt% of homogeneously distributed graphene, electrical conductivity could be improved up to four times (Wei *et al.*, 2015). The mechanical properties of 3D printed specimens are strongly dependent on the printing orientation (Wu *et al.*, 2020; Yamamoto *et al.*, 2019). The filament uniformity is another crucial parameter for achieving the high quality of the printed part. The incorporation of small contents of nanofiller can remarkably change the rheological behavior of the polymer, which is vital in the filament extrusion process (Yamamoto *et al.*, 2019). Also, the homogenous dispersion of the nanoparticles is significant for achieving the highest possible properties. Nanoparticles can remarkably affect the rheology of the polymer in the molten state and is a dominant factor influencing the printability (Wu *et al.*, 2020; Zheng *et al.*, 2006). On the other hand, during the manufacture of PMCs, the problems associated with agglomeration and poor interfacial bondage of nanoparticles with polymers could be faced. Chemical or thermal surface treatment can overcome these challenges (Saroia *et al.*, 2020). In a research conducted by Zheng *et al.* (2006) the reinforced and non-reinforced specimens of polystyrene were evaluated, and enhancements in reinforced samples were reported especially increasing of about 300% in tensile strength compared to the non-reinforced samples. Chizari *et al.* (2016) fabricated a type of 3D printed conductive material by blending CNTs and PLA in the ball mill. Various contents of CNTs were mixed with PLA to evaluate the effect of the reinforcement concentration on conductivity. The results showed that with increasing CNTs concentration, the conductivity of the resulted composite was improved, but the clogging of the nozzle was also observed. Dichloromethane was used as a solvent for dissolving dried forms of CNTs and PLA uniformly and printed through the 3D printing process. The electrical conductivity of fabricated specimens was higher than the other conductive 3D printed PMCs (Chizari *et al.*, 2016). With the help of nanotechnology, AM is used in different applications, which have been described in the following sections.

Applications of Additively Manufactured PMCs

Medical Applications

Recently, 3D printing in tissue engineering applications, including medical devices and scaffolds, regenerative medicine, ex-vivo tissues, and drug delivery, have attracted intense attention (Singh and Ramakrishna, 2017). Various applied PMCs with their relevant AM processes that have been used in biomedical applications are summarized in Table 3.

For scaffolds, providing cell infiltration and proliferation is a vital requirement for physical connection. Conventional manufacturing methods have the poor ability to incorporate internal architecture and controlling the porosity of the scaffold. Applying AM processes can solve these issues by their capability to control the pore size and pore distribution in the fabricated scaffold

Table 2 Summary of the results for polymer matrix composites (PMCs) reinforced by nanomaterials fabricated by various methods including 3D printing

<i>Polymeric matrix</i>	<i>Reinforcement nanomaterial</i>	<i>Fabrication method</i>	<i>Results</i>	<i>References</i>
Ethylene/1-octene copolymers (EOCs)	CNT	Hot pressing	Increasing thermal conductivity	Yan et al. (2016)
PMMA-Mon	CNT	Casting	Suitable mechanical properties and supporting osteoblast cells	Pahlevanzadeh et al. (2019b)
Polypropylene (PP) strands	Liquid crystalline polymer (TLCP) fibrils	FDM	Revealing that monofilaments tensile properties is dependent on diameter of capillary	Gray et al. (1998) , Sengupta et al. (2011)
PMMA-PCL	Baghdadite	Casting	Great mechanical properties, and favorable cytocompatibility	Pahlevanzadeh et al. (2019a)
PMMA-PCL	Fluorapatite	Casting	Proper mechanical properties, favorable bioactivity and high MG63 cells viability	Pahlevanzadeh et al. (2018)
Epoxy resin	Carbon-coated nickel nanoparticles	Using electrostatic generator and molding	Dielectric constant increasing	Zhang et al. (2006)
Polyurethane	GNPs	Bioprinting	Increased the oxygen metabolism (2–4 times more) and enhancement of neural differentiation	Huang et al. (2017)
ABS	GNPs	Extrusion based printer	Demonstrating a printable form of graphene composite containing up to 5.6 wt% graphene for the first time	Wei et al. (2015)
Polystyrene	Nano- Al_2O_3	SLS	Increasing the notched impact strength and tensile strength	Zheng et al. (2006)
PLA	CNT	Extrusion based printer	Suitable construct for different applications like various types of sensors	Chizari et al. (2016)
PLA	CNT	Direct writing	Excellent sensitivity	Guo et al. (2015)
PLA	Silver nanowire	FDM	Indicate high antibacterial effect against both <i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	Bayraktar et al. (2019)
PLA	Clay	FDM	Increase storage modulus and thermal stability	Coppola et al. (2018)
PLA	GNPs	FDM	Enhance the tensile and flexural strength and suitable biocompatibility	Wang et al. (2020)
PLA	CNT	Solvent-cast 3D printing	Functional optimization of light-weight and semi-transparent EMI shields	Chizari et al. (2017)
PLA	Graphene	FDM	Enhance the mechanical and thermomechanical properties	Prashantha and Roger (2017)
PLA/PU	GO	FDM	Improved the mechanical property, thermal stability and indicating good biocompatibility	Chen et al. (2017)
Epoxy acrylate	TiO ₂	SLA	Introduce a low-cost method to improve the performance of the photosensitive resin	Yugang et al. (2011)
ABS	Graphene	FDM	A graphene composite, with a graphene (up to 5.6 wt%), can be 3D printable into CAD for the first time	Wei et al. (2015)
Polystyrene	Al_2O_3	SLS	Provides a theoretical and technical basis for the production of nano- Al_2O_3 / polystyrene products	Zheng et al. (2006)

Table 3 Applied polymer matrix composites for biomedical applications

<i>Polymeric matrix</i>	<i>Additive</i>	<i>Fabrication method</i>	<i>Application</i>	<i>References</i>
PLA	HA	3D plotting	Bone repair	Zhang et al. (2016)
PLA	HA	FDM	Trabecular bone replacement	Senatov et al. (2016)
PLA/PEG	Bioglass	3D plotting	Tissue engineering	Serra et al. (2013)
PLA/PEG	HA	FDM	Tissue engineering	Kutikov et al. (2015)
PLA/CS	HA	FDM	Bone repair	Rogina et al. (2016)
Alginate	TCP	3D plotting	Bone repair	Diogo et al. (2014)
Alginate	CNT	3D plotting	Tissue engineering	Yildirim et al. (2008)
Al/collagen	Silica	3D plotting	Hard tissue regeneration	Lee et al. (2014)
SA/gelatin	HA	3D plotting	Bone repair	Wang et al. (2016)
CS	CP	Robocasting	Bone repair	Caballero et al. (2019)
CS	nBA	Robocasting	Bone repair	Dorj et al. (2012)

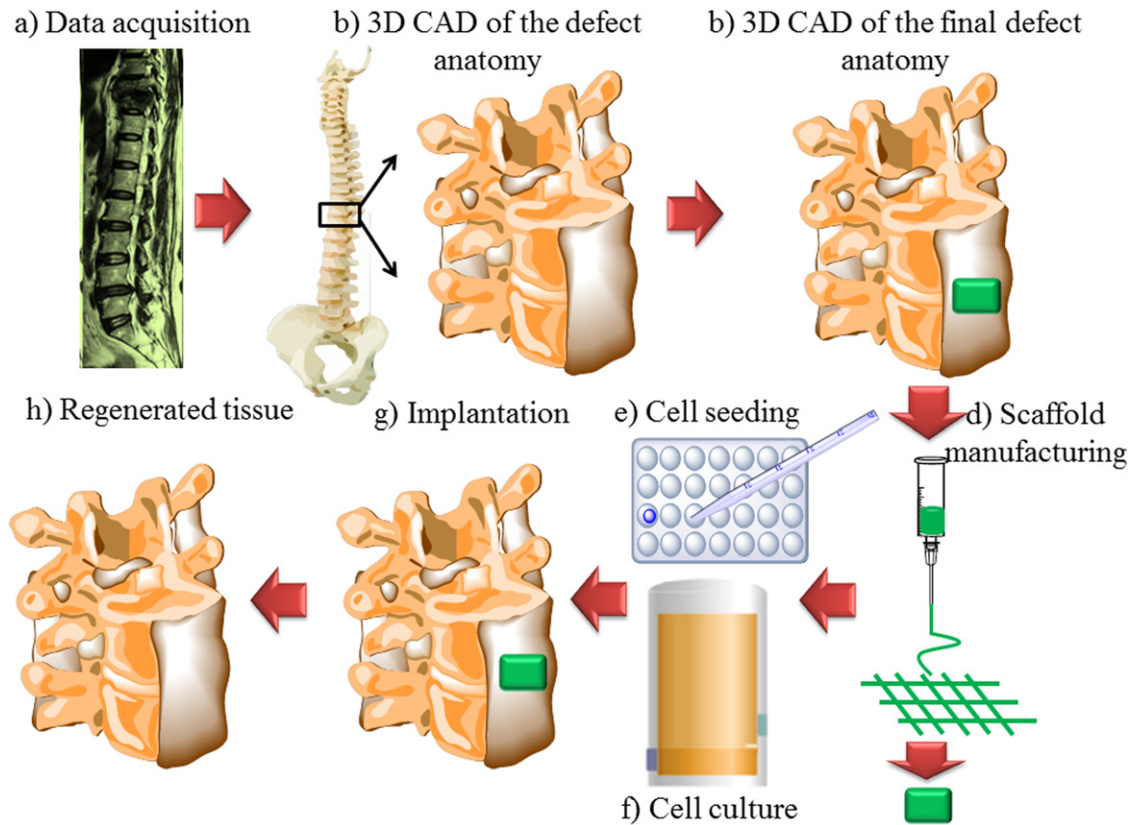


Fig. 9 Schematic illustration of different development steps of tissue engineering scaffolds including: (a) data acquisition by the medical imaging techniques; (b, c) processing the derived data by CAD and CAM software and designing the customized scaffold; (d) AM manufacturing of the scaffold; (e, f) cell seeding and culturing; (g) implantation of the AM fabricated scaffold; (h) tissue regeneration.

(Kumar and Kruth, 2010). Tissue engineering aims to develop the temporary 3D components for applying to promote the process of natural healing of damaged tissues. The natural polymers and their composites, as one of the biomaterial categories, have been broadly investigated due to their capability to reproduce the perfect 3D extracellular environment for the growth of the tissue. The 3D components with a customized designed geometry with different sizes and shapes and having a fully interconnected network of pores could be fabricated by AM methods. CAD data for the development of scaffolds could be derived from diagnostic medical images, like CT and MRI, typically treated by CAD and CAM software. The process of AM manufacturing of tissue engineering scaffolds has been illustrated in Fig. 9. The bio-inks that are applied in bio-printing have an influential role in fabricating regenerative medicine (Mota *et al.*, 2015). The 3D bioprinting is known as an AM process that can be applied for manufacturing the customized structures for using to repair the damaged tissues or organs (Huang *et al.*, 2017 and Bishop *et al.*, 2017). Fig. 10 represents bio-printing process overview in order to better understanding how to combine the 3D printing method for a polymeric matrix with live cells.

The 3D printed PMCs have been mostly used in the field of hard tissue regeneration. For example, Dorj *et al.* (2012) reinforced the chitosan matrix with a bioglass bioactive reinforcement agent for the robocasting 3D printing process. Their outcomes revealed that the composite scaffold containing 10 wt% nano bioactive glass presented a bimodal structure, including macro and micro-structures. In their process, the solution of the composite was rapidly solidified when the samples were placed into a dry-ice tank. The manufactured chitosan/10 wt% nano bio-glass scaffold showed high bioactivity and good cell attachment properties. In another research, Caballero *et al.* (2019) reinforced chitosan with suspensions of Ca-P particles in acidic aqueous solution in the robocasting process for fabricating chitosan/Ca-P scaffolds. The study results revealed that rheological properties of combination might be adjusted by changing the composition in which more printable inks were achieved with higher amounts of chitosan.

3D printed PMCs have been successfully used in soft tissue engineering and drug/growth factor delivery. Xiong *et al.* (2017) presented the AM fabricated gelatin-sulfonated silk composite scaffold, incorporated with basic fibroblast growth factor 2 (FGF-2) via binding with a sulfonic acid group (SO₃) (3DG-SF-SO₃-FGF). Modified silk fibroin with sulfonated moieties was applied in the scaffold to improve its hydrophilicity and facilitate the incorporation of FGF-2. They showed that the immobilized growth factor FGF-2 can exhibit sustained release kinetics and can stimulate *in vitro* cell proliferation and migration. The AM fabricated scaffold displayed promising results when applied to treat full-thickness cutaneous injuries in an animal model. The outcomes showed that the incorporation of FGF-2 in the scaffold improved the rate of proliferation from about 40% to approximately 75%, tissue morphology, collagen fibril assembly, blood vessel formation, and expression of different corresponding markers.

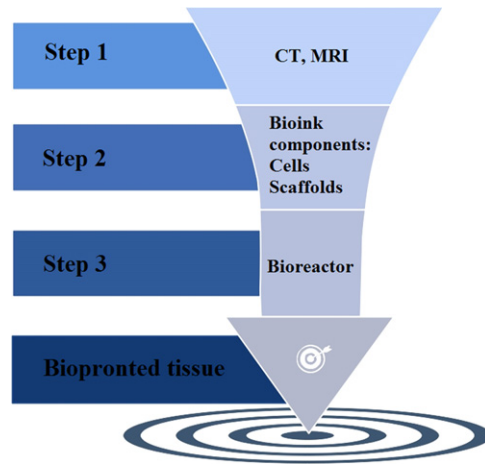


Fig. 10 Process chart of bio-printing.

Orthopedics is one of the well-known fields in which 3D printed PMCs are applied (Choi and Kim, 2015; Haleem *et al.*, 2018; Leigh *et al.*, 2012). The AM technology is used for fabricating anatomic models, surgical instruments, tool design, splints, implants, and prosthesis using various types of materials like nylons, polymers, and even metals. In orthopedics, the customized analysis of the patient, using medical images, is vital for obtaining precise data (Javaid and Haleem, 2018a; Cooperstein *et al.*, 2015).

Besides, 3D printing has the potential to help the cardiologists and cardiac surgeons. The 3D model of the customized heart for a specific patient could be fabricated by AM in a short time and with a comparatively low cost. In this way, before performing the actual surgery on the patient, the 3D model is created and analyzed. This process could improve the treatment results of the patients and saving their lives (Haleem *et al.*, 2018). The materials that could be used for 3D printing of the components of the artificial heart are plastic, powder, metal, and composites (Haleem *et al.*, 2018).

Electronics Applications

The electronic components or devices that have the ability to control and amplify the electric charges are called active electronic components (Saengchairat *et al.*, 2017). Different subtractive traditional manufacturing processes have been broadly used for fabricating active electronic components typically based on photolithography, which has many drawbacks, including complicated and expensive setup, hazardous chemical preparation, and a significant wastage quantity of rare-earth material (Saengchairat *et al.*, 2017). The AM techniques, which have apparent advantages comparing with the traditional processes like decreasing in material wastage, less fabrication time, and lower setup cost, can solve the mentioned disadvantages. Lately, many studies have been conducted on the 3D printing of various electronic sensors. Leigh *et al.* manufactured different sensors, including piezoresistive and capacitive types, applying the FDM process utilizing carbon black reinforced PCL composite (Leigh *et al.*, 2012). The piezoresistive sensors showed their ability to detect the mechanical flexing based on the variation of the electrical resistance. In the same way, the capacitive sensors that were 3D printed on the customized fabricated devices like 3D smart vessels, which can sense the presence of water based on the changes of capacitance (Leigh *et al.*, 2012).

In recent years, some studies have tried to fabricate the 3D printed, electronic components. A connector for an electrical circuit was 3D printed, applying a digital light process using the material of silver and cross-linked photopolymer (Cooperstein *et al.*, 2015). The fabricated 3D porous structure utilizing the printable oil-in-water emulsion was dipped in a dispersion of silver nanoparticles, then sintered to attain conductive percolation paths. The porosity and total surface area of the 3D printed part could be controlled by changing the parameters of the process. Therefore, the electrical conductivity could be potentially designed.

Some studies have also tried to 3D print the electronic components by encapsulating the metallic wires into a polymeric matrix. This method of 3D printing is similar to the utilized method for fabricating continuous fiber-reinforced PMCs. Molten styrene block copolymers and Cu wires were individually supplied and co-extruded. The printed two-phase composites were confirmed to be used as an open membrane switch (Saari *et al.*, 2015), which is activated when the membrane is deformed by pressure contact, resulting in the Cu wires on adjacent polymer layers to be shorted together.

The other application of AM in electronics is fabricating the supercapacitors. Tanwilaisiri *et al.* (2018) tried to fabricate a novel multi-material electrochemical supercapacitors using a combined AM manufacturing process, including FDM and DIW. The results of the research showed that the fabrication process has an outstanding perspective on the manufacturing of other 3D printed electrochemical devices (Tanwilaisiri *et al.*, 2018). The concept of green energy, because of its advantages, including cost-effectiveness and pollution-free aspects, has attracted the attention of many researchers. AM technology has various applications in the field of green energy. As a self-powered electronics component, TENG is a unique and practical usage of green energy. Qiao *et al.* (2018) applied the FDM process for fabricating a type of TENG, which could generate green energy from the vibrations in environmental conditions. They investigated different factors, including input power, excitation frequencies, and current zigzag

patterns, which had a direct or indirect effect on the efficiency of TENG. The efficiency of their designed TENG in the mode of vertical contact separation was documented up to about 64% (Qiao *et al.*, 2018).

Aerospace Applications

The AM technology has been accepted in the aerospace industry due to many advantages that are described below. Firstly, the potential to a remarkable reduction of “buy to fly ratio”, which is defined as the ratio of the mass of required material for fabricating a component to the final mass of the component that flies on the airplane. This ratio could be as high as 20:1 for some aerospace components fabricated by conventional manufacturing processes. For the AM fabricated parts, this ratio is approximately one. The effective usage of the material is often an essential concern for numerous aerospace applications (Horn and Harrysson, 2012). Many research organizations are discovering the possible routes to use the AM technology to fabricate PMCs that can be used in aerospace applications because of the likely cost-effectiveness resulting in reducing fuel consumption (Wang *et al.*, 2017). SLS and EBM methods can make the fabrication process more comfortable and more cost-effective. Secondly, the capability of using carbon fiber reinforced PMCs for fabricating the high precision and geometrically complicated airfoils, blades, propellers, etc (Saroia *et al.*, 2020; Invernizzi *et al.*, 2016). The AM fabricated metallic alloys have been applied for many parts in the aerospace industry, such as turbine blades and engine exhaust because metals have higher strength for sustaining at elevated temperatures than the plastics (Goh *et al.*, 2017).

Nevertheless, the plastics could also be an alternative option for the AM fabrication of propellers and wind turbine blades due to their lower weight and more cost-effectiveness than the metals. Some polymers have been developed in recent years that can resist high temperatures, which can be applied in many aerospace applications. A plastic material containing chopped carbon fiber and a type of thermoplastic heat-resistant polyetherimide polymer has been developed, which can resist the temperatures up to about 205°C and can be used for fabricating the inlet guide vanes using the FDM process (Misra *et al.*, 2015).

The AM has been proved as an innovative technology in the aerospace industry. Many companies that manufacture airplanes are using 3D printing methods to reduce the weight and manufacturing time of different functional parts. The PBF method, as an AM process, offers the fabrication of the small parts with high accuracy. The PBF method has the potential to give a high degree of freedom to the manufacturer for design optimization and its functional attributes. The brackets of Airbus A350 XMB were fabricated using the PBF process. The manufactured parts had a 30% lower weight, and the manufacturing time was also reduced up to 75%, compared with the conventional fabrication processes (Wang *et al.*, 2017).

Benefits, Limitations, and Future Trends

In recent years, various AM techniques using different material types, including thermoplastic polymers, metals, and ceramics matrix, reinforced with many reinforcements such as metallic nanoparticles, fibers, and various conductive materials, which can improve their functionality, have been applied. Choosing the material depends on the applied AM technology and the properties needed for the product (Saroia *et al.*, 2020).

Despite the enhancement that can be achieved by using nanoparticles for reinforcing in composites, they may decline the formability of the fabricated nanocomposites (Weng *et al.*, 2016; Coppola *et al.*, 2017). Decreasing in ductility could be attributed to two main reasons: (1) inadequate interfacial bonding of the reinforcement and matrix, and (2) clustering of nanoparticles, which can act as stress concentrating defects (De Mori *et al.*, 2018). Besides, the loading of reinforcements is limited to a specific quantity that is called the threshold point. For the amounts higher than that point, the reinforcement particles start to agglomerate and form the voids, resulting in declining mechanical properties (Saroia *et al.*, 2020). Chemical or thermal surface treatments (Zheng *et al.*, 2006; Kim *et al.*, 2013) could be applied before printing to solve these issues. AM techniques are applied in many industries in different ways. The aerospace and automotive industries allow manufacturing the lightweight components with complicated geometries such as honeycomb cell and the parts containing cavities and angle cuttings for decreasing the specific strength. Besides, educational models for studying the physical concepts and visualization could be developed by 3D printing. The other field that can extensively use 3D printed components is biomedical because of the ability of AM methods for accurate adjustment of porosity shape and size, fiber size, appropriate interconnectivity of the pores, and fabrication of customized components for the patients. For instance, different advantages have been caused by using the 3D printing process to fabricate the heart components in cardiology applications. For describing the process to the patient, the anatomical 3D model is also useful for better understanding. Besides, the 3D printed model can be used for training prior to surgery, increasing the possibility of saving lives, improving results, and offering new treatments (Haleem *et al.*, 2018).

Despite remarkable improvements of PMCs additive manufacturing in recent years because of facilitating the customized production of strong, lightweight products which allows designs that were not possible with conventional fabricating processes, it is still not widely accepted by most industries. There are many drawbacks to AM technology that should be solved. For instance, the wide application of 3D printing is strictly limited by printable materials. Although reinforcements can enhance the performance of 3D printed PMCs, compared to the PMCs fabricated by conventional methods using molding, most of the printed composites still have lower mechanical properties and are not able to meet the functional requirement (Wang *et al.*, 2017). The other problem is that, in many cases, the fabrication cost of the parts using AM processes is much more than that of conventional processes (Thomas and

Gilbert, 2014), as the most AM processes are time-consuming now, and fabricating the parts with large size is difficult (De Mori *et al.*, 2018). Besides, the implants that fabricated by need high cost for design. The other problem of AM technology is the required time for preparing the physical model. It depends on the level of complexity and size of the model. The acquisition and processing of data based on the images take a long time. Then for the fabrication of the model, it depends on the types of technologies of AM. In some cases, it is not implemented and can only be used to better understand the actual surgery (Javaid and Haleem, 2018b). Normally, the fabrication of scaffolds that successfully mimic the structural and mechanical characteristics of the target tissue is a complicated process. On the other hand, monolithic polymers do not show good mechanical properties, especially in hard tissue engineering applications (De Mori *et al.*, 2018). So it seems that AM made PMCs are promising materials for tissue engineering and regenerative medicine because of their adjustable properties (Joseph *et al.*, 2012; De Mori *et al.*, 2018). Since all kinds of cells require a network of vessels to gain access to nutrients and oxygen and expel unwanted products, vascularization is a vital matter. For that reason, the formation of a complete complex vascularization network in PMCs printed-specimens for fabricating full organ is remaining a secret (Mironov *et al.*, 2009).

Lastly, it should be mentioned that most of the challenges in AM technology are dependent on the process. For example, choosing the best binder in 3D printing is considered one of the difficulties in the BJ process (Sahranavard *et al.*, 2020). As previously stated, further studies on chemical or thermal surface treatment are required to fabricate the PMCs with a uniform dispersion of reinforcements and, consequently, adequate mechanical properties. Generally, enhancing the mechanical properties of the PMCs could be attained through uniform distribution of fiber, particle, or nanomaterial reinforcements in the polymeric matrix for tissue engineering and wound healing applications (Hadisi *et al.*, 2020; Bakhsheshi-Rad *et al.*, 2017, 2019, 2020; Parham *et al.*, 2020; Pahlevanzadeh *et al.*, 2020b). Also, the reduction in cost and fabrication time in AM processes may result in using the AM in the production of the parts with large size.

Conclusion

The AM technology has a remarkable impact on the modern world, and despite many challenges and disadvantages, its applications have been increased with various potentials, especially for fabricating polymer matrix composites (PMCs) due to their adjustable and excellent properties such as high specific strength, good resistance against corrosion, abrasion, impact, fatigue, and fracture. As discussed in this chapter, many signs of progress have been made in developing 3D printing of PMCs, including improving properties and their applications in aerospace, electronics, and biomedical industries. It is worth noting that some remarkable problems such as agglomeration of reinforcement, the formation of voids, time-consuming, and low mechanical properties should be solved in 3D printed PMCs. Finally, some advantages and disadvantages were pointed out for supplementary studies on 3D printed PMCs.

References

- Apelgren, P., Amoroso, M., Lindahl, A., *et al.*, 2017. Chondrocytes and stem cells in 3D-bioprinted structures create human cartilage in vivo. *PLOS One* 12 (12), e0189428.
- Au, A.K., Huynh, W., Horowitz, L.F., Folch, A., 2016. 3D-printed microfluidics. *Angewandte Chemie International Edition* 55 (12), 3862–3881.
- Avila, A.F., Rodrigues, P.C., Santos, D.B., Faria, A.C., 2003. A dual analysis for recycled particulate composites: Linking micro-and macro-mechanics. *Materials Characterization* 50 (4–5), 281–291.
- Bakhsheshi-Rad, H.R., Hadisi, Z., Hamzah, E., *et al.*, 2017. Drug delivery and cytocompatibility of ciprofloxacin loaded gelatin nanofibers-coated Mg alloy. *Materials Letters* 207, 179–182.
- Bakhsheshi-Rad, H.R., Ismail, A.F., Aziz, M., *et al.*, 2019. Antibacterial activity and in vivo wound healing evaluation of polycaprolactone-gelatin methacryloyl-cephalexin electrospun nanofibrous. *Materials Letters* 256, 126618.
- Bakhsheshi-Rad, H.R., Hadisi, Z., Ismail, A.F., *et al.*, 2020. In vitro and in vivo evaluation of chitosan-alginate/gentamicin wound dressing nanofibrous with high antibacterial performance. *Polymer Testing* 82, 106298.
- Balla, V.K., Kate, K.H., Satyavolu, J., Singh, P., Tadimet, J.G.D., 2019. Additive manufacturing of natural fiber reinforced polymer composites: Processing and prospects. *Composites Part B: Engineering* 174, 106956.
- Bayraktar, I., Doganay, D., Coskun, S., *et al.*, 2019. 3D printed antibacterial silver nanowire/poly(lactide) nanocomposites. *Composites Part B: Engineering* 172, 671–678.
- Bekas, D.G., Hou, Y., Liu, Y., Panesar, A., 2019. 3D printing to enable multifunctionality in polymer-based composites: a review. *Composites Part B: Engineering* 179, 107540.
- Bendtsen, S.T., Quinell, S.P., Wei, M., 2017. Development of a novel alginate-poly(vinyl alcohol)-hydroxyapatite hydrogel for 3D bioprinting bone tissue engineered scaffolds. *Journal of Biomedical Materials Research Part A* 105 (5), 1457–1468.
- Bishop, E.S., Mostafa, S., Pakvasa, M., *et al.*, 2017. 3-D bioprinting technologies in tissue engineering and regenerative medicine: Current and future trends. *Genes & Diseases* 4 (4), 185–195.
- Brenken, B., Barocio, E., Favaloro, A., Kunc, V., Pipes, R.B., 2018. Fused filament fabrication of fiber-reinforced polymers: A review. *Additive Manufacturing* 21, 1–16.
- Caballero, S.S.R., Saiz, E., Montebault, A., *et al.*, 2019. 3-D printing of chitosan-calcium phosphate inks: Rheology, interactions and characterization. *Journal of Materials Science: Materials in Medicine* 30 (1), 6.
- Carneiro, O.S., Silva, A.F., Gomes, R., 2015. Fused deposition modeling with polypropylene. *Materials & Design* 83, 768–776.
- Chen, Q., Mangadlao, J.D., Wallat, J., *et al.*, 2017. 3D printing biocompatible polyurethane/poly (lactic acid)/graphene oxide nanocomposites: Anisotropic properties. *ACS Applied Materials & Interfaces* 9 (4), 4015–4023.
- Chizari, K., Daoud, M.A., Ravindran, A.R., Theriault, D., 2016. 3D printing of highly conductive nanocomposites for the functional optimization of liquid sensors. *Small* 12 (44), 6076–6082.
- Chizari, K., Arjmand, M., Liu, Z., Sundararaj, U., Theriault, D., 2017. Three-dimensional printing of highly conductive polymer nanocomposites for EMI shielding applications. *Materials Today Communications* 11, 112–118.
- Choi, J.W., Kim, N., 2015. Clinical application of three-dimensional printing technology in craniofacial plastic surgery. *Archives of Plastic Surgery* 42 (3), 267.

- Chung, D.D.L., 2001. Materials for thermal conduction. *Applied Thermal Engineering* 21 (16), 1593–1605.
- Compton, B.G., Lewis, J.A., 2014. 3D-printing of lightweight cellular composites. *Advanced Materials* 26 (34), 5930–5935.
- Cooperstein, I., Layani, M., Magdassi, S., 2015. 3D printing of porous structures by UV-curable O/W emulsion for fabrication of conductive objects. *Journal of Materials Chemistry C* 3 (9), 2040–2044.
- Coppola, B., Cappetti, N., Di Maio, L., Scarfato, P., Incarnato, L., 2017. Layered silicate reinforced polylactic acid filaments for 3D printing of polymer nanocomposites. In *Proceedings of the IEEE 3rd International Forum on Research and Technologies for Society and Industry (RTSI)*. IEEE, pp. 1–4.
- Coppola, B., Cappetti, N., Di Maio, L., Scarfato, P., Incarnato, L., 2018. 3D printing of PLA/clay nanocomposites: Influence of printing temperature on printed samples properties. *Materials* 11 (10), 1947.
- De Gans, B.J., Duineveld, P.C., Schubert, U.S., 2004. Inkjet printing of polymers: State of the art and future developments. *Advanced Materials* 16 (3), 203–213.
- de Leon, A.C., Chen, Q., Palaganas, N.B., *et al.*, 2016. High performance polymer nanocomposites for additive manufacturing applications. *Reactive and Functional Polymers* 103, 141–155.
- De Mori, A., Peña Fernández, M., Blunn, G., Tozzi, G., Roldo, M., 2018. 3D printing and electrospinning of composite hydrogels for cartilage and bone tissue engineering. *Polymers* 10 (3), 285.
- Diogo, G.S., Gaspar, V.M., Serra, I.R., Fradique, R., Correia, I.J., 2014. Manufacture of β -TCP/alginate scaffolds through a Fab@ home model for application in bone tissue engineering. *Biofabrication* 6 (2), 025001.
- Dorj, B., Park, J.H., Kim, H.W., 2012. Robocasting chitosan/nanobioactive glass dual-pore structured scaffolds for bone engineering. *Materials Letters* 73, 119–122.
- Fina, F., Goyanes, A., Gaisford, S., Basit, A.W., 2017. Selective laser sintering (SLS) 3D printing of medicines. *International Journal of Pharmaceutics* 529 (1–2), 285–293.
- Francis, V., Jain, P.K., 2015. Advances in nanocomposite materials for additive manufacturing. *International Journal of Rapid Manufacturing* 5 (3–4), 215–233.
- Gaytan, S.M., Cadena, M.A., Karim, H., *et al.*, 2015. Fabrication of barium titanate by binder jetting additive manufacturing technology. *Ceramics International* 41 (5), 6610–6619.
- Goh, G.D., Agarwala, S., Goh, G.L., *et al.*, 2017. Additive manufacturing in unmanned aerial vehicles (UAVs): Challenges and potential. *Aerospace Science and Technology* 63, 140–151.
- Gray IV, R.W., Baird, D.G., Bøhn, J.H., 1998. Thermoplastic composites reinforced with long fiber thermotropic liquid crystalline polymers for fused deposition modeling. *Polymer Composites* 19 (4), 383–394.
- Guo, S.Z., Yang, X., Heuzey, M.C., Theriault, D., 2015. 3D printing of a multifunctional nanocomposite helical liquid sensor. *Nanoscale* 7 (15), 6451–6456.
- Guvendiren, M., Molde, J., Soares, R.M., Kohn, J., 2016. Designing biomaterials for 3D printing. *ACS Biomaterials Science & Engineering* 2 (10), 1679–1693.
- Hadisi, Z., Farokhi, M., Bakhsheshi-Rad, H.R., *et al.*, 2020. Hyaluronic acid (HA)-based Silk Fibroin/Zinc oxide core-shell electrospun dressing for burn wound management. *Macromolecular Bioscience* 19, 1900328.
- Haleem, A., Javaid, M., Saxena, A., 2018. Additive manufacturing applications in cardiology: A review. *The Egyptian Heart Journal* 70 (4), 433–441.
- Hao, W., Liu, Y., Zhou, H., Chen, H., Fang, D., 2018. Preparation and characterization of 3D printed continuous carbon fiber reinforced thermosetting composites. *Polymer Testing* 65, 29–34.
- Heidari-Rarani, M., Rafiee-Afarani, M., Zahedi, A.M., 2019. Mechanical characterization of FDM 3D printing of continuous carbon fiber reinforced PLA composites. *Composites Part B: Engineering* 175, 107147.
- Horn, T.J., Harrysson, O.L., 2012. Overview of current additive manufacturing technologies and selected applications. *Science Progress* 95 (3), 255–282.
- Horvath, J., 2014. A brief history of 3D printing. In *Mastering 3D Printing*. Berkeley, CA: Apress, pp. 3–10.
- Huang, C.T., Shrestha, L.K., Ariga, K., Hsu, S.H., 2017. A graphene-polyurethane composite hydrogel as a potential bioink for 3D bioprinting and differentiation of neural stem cells. *Journal of Materials Chemistry B* 5 (44), 8854–8864.
- Hwang, S., Reyes, E.I., Moon, K.S., Rumpf, R.C., Kim, N.S., 2015. Thermo-mechanical characterization of metal/polymer composite filaments and printing parameter study for fused deposition modeling in the 3D printing process. *Journal of Electronic Materials* 44 (3), 771–777.
- Invernizzi, M., Natale, G., Levi, M., Turri, S., Griffini, G., 2016. UV-assisted 3D printing of glass and carbon fiber-reinforced dual-cure polymer composites. *Materials* 9 (7), 583.
- Javaid, M., Haleem, A., 2018a. Additive manufacturing applications in medical cases: A literature based review. *Alexandria Journal of Medicine* 54 (4), 411–422.
- Javaid, M., Haleem, A., 2018b. Additive manufacturing applications in orthopaedics: A review. *Journal of Clinical Orthopaedics and Trauma* 9 (3), 202–206.
- Joseph, K., Malhotra, S.K., Goda, K., Sreekala, M.S., 2012. *Polymer Composites, Macro- and Microcomposites*. vol. 1. John Wiley & Sons.
- Kesti, M., Eberhardt, C., Paggiaccia, G., *et al.*, 2015. Bioprinting complex cartilaginous structures with clinically compliant biomaterials. *Advanced Functional Materials* 25 (48), 7406–7417.
- Kim, H.C., Hahn, H.T., Yang, Y.S., 2013. Synthesis of PA12/functionalized GNP nanocomposite powders for the selective laser sintering process. *Journal of Composite Materials* 47 (4), 501–509.
- Kruth, J.P., Wang, X., Laoui, T., Froyen, L., 2003. Lasers and materials in selective laser sintering. *Assembly Automation* 23 (4), 357–371.
- Kumar, S., Kruth, J.P., 2010. Composites by rapid prototyping technology. *Materials & Design* 31 (2), 850–856.
- Kutikov, A.B., Gurijala, A., Song, J., 2015. Rapid prototyping amphiphilic polymer/hydroxyapatite composite scaffolds with hydration-induced self-fixation behavior. *Tissue Engineering Part C: Methods* 21 (3), 229–241.
- Lebel, L.L., Aissa, B., Khakani, M.A.E., Theriault, D., 2010. Ultraviolet-assisted direct-write fabrication of carbon nanotube/polymer nanocomposite microcoils. *Advanced Materials* 22 (5), 592–596.
- Lee, H., Kim, Y., Kim, S., Kim, G., 2014. Mineralized biomimetic collagen/alginate/silica composite scaffolds fabricated by a low-temperature bio-plotting process for hard tissue regeneration: Fabrication, characterisation and in vitro cellular activities. *Journal of Materials Chemistry B* 2 (35), 5785–5798.
- Leigh, S.J., Bradley, R.J., Purcell, C.P., Billson, D.R., Hutchins, D.A., 2012. A simple, low-cost conductive composite material for 3D printing of electronic sensors. *PLOS One* 7 (11), e49365.
- Lewicki, J.P., Rodriguez, J.N., Zhu, C., *et al.*, 2017. 3D-printing of meso-structurally ordered carbon fiber/polymer composites with unprecedented orthotropic physical properties. *Scientific Reports* 7 (1), 1–14.
- Lewis, J.A., 2006. Direct ink writing of 3D functional materials. *Advanced Functional Materials* 16 (17), 2193–2204.
- Li, J., Wu, C., Chu, P.K., Gelinsky, M., 2020. 3D printing of hydrogels: Rational design strategies and emerging biomedical applications. *Materials Science and Engineering: R: Reports* 140, 100543.
- Li, N., Li, Y., Liu, S., 2016. Rapid prototyping of continuous carbon fiber reinforced polylactic acid composites by 3D printing. *Journal of Materials Processing Technology* 238, 218–225.
- Manapat, J.Z., Chen, Q., Ye, P., Advincula, R.C., 2017. 3D printing of polymer nanocomposites via stereolithography. *Macromolecular Materials and Engineering* 302 (9), 1600553.
- Markstedt, K., Mantas, A., Tournier, I., *et al.*, 2015. 3D bioprinting human chondrocytes with nanocellulose–alginate bioink for cartilage tissue engineering applications. *Biomacromolecules* 16 (5), 1489–1496.
- Masood, S.H., Song, W.Q., 2004. Development of new metal/polymer materials for rapid tooling using fused deposition modelling. *Materials & Design* 25 (7), 587–594.
- Matsuzaki, R., Ueda, M., Namiki, M., *et al.*, 2016. Three-dimensional printing of continuous-fiber composites by in-nozzle impregnation. *Scientific Reports* 6, 23058.
- Mironov, V., Visconti, R.P., Kasyanov, V., *et al.*, 2009. Organ printing: Tissue spheroids as building blocks. *Biomaterials* 30 (12), 2164–2174.
- Misra, A.K., Grady, J.E., Carter, R., 2015. *Additive Manufacturing of Aerospace Propulsion Components*.
- Mondschein, R.J., Kanitkar, A., Williams, C.B., Verbridge, S.S., Long, T.E., 2017. Polymer structure-property requirements for stereolithographic 3D printing of soft tissue engineering scaffolds. *Biomaterials* 140, 170–188.

- Moon, J., Grau, J.E., Knezevic, V., Cima, M.J., Sachs, E.M., 2002. Ink-jet printing of binders for ceramic components. *Journal of the American Ceramic Society* 85 (4), 755–762.
- Mota, C., Puppi, D., Chiellini, F., Chiellini, E., 2015. Additive manufacturing techniques for the production of tissue engineering constructs. *Journal of Tissue Engineering and Regenerative Medicine* 9 (3), 174–190.
- Ngo, T.D., Kashani, A., Imbalzano, G., Nguyen, K.T., Hui, D., 2018. Additive manufacturing (3D printing): A review of materials, methods, applications and challenges. *Composites Part B: Engineering* 143, 172–196.
- Nikzad, M., Masood, S.H., Sbarski, I., 2011. Thermo-mechanical properties of a highly filled polymeric composites for fused deposition modeling. *Materials & Design* 32 (6), 3448–3456.
- Ning, F., Cong, W., Qiu, J., Wei, J., Wang, S., 2015. Additive manufacturing of carbon fiber reinforced thermoplastic composites using fused deposition modeling. *Composites Part B: Engineering* 80, 369–378.
- Nonato, R.C., Mei, L.H.I., Bonse, B.C., Chinaglia, E.F., Morales, A.R., 2019. Nanocomposites of PLA containing ZnO nanofibers made by solvent cast 3D printing: Production and characterization. *European Polymer Journal* 114, 271–278.
- Pahlevanzadeh, F., Bakhsheshi-Rad, H.R., Hamzah, E., 2018. In-vitro biocompatibility, bioactivity, and mechanical strength of PMMA-PCL polymer containing fluorapatite and graphene oxide bone cements. *Journal of the Mechanical Behavior of Biomedical Materials* 82, 257–267.
- Pahlevanzadeh, F., Bakhsheshi-Rad, H.R., Ismail, A.F., Aziz, M., 2019a. Apatite-forming ability, cytocompatibility, and mechanical properties enhancement of poly methyl methacrylate-based bone cements by incorporating of baghdadite nanoparticles. *International Journal of Applied Ceramic Technology* 16 (5), 2006–2019.
- Pahlevanzadeh, F., Bakhsheshi-Rad, H.R., Ismail, A.F., Aziz, M., Chen, X.B., 2019b. Development of PMMA-Mon-CNT bone cement with superior mechanical properties and favorable biological properties for use in bone-defect treatment. *Materials Letters* 240, 9–12.
- Pahlevanzadeh, F., Emadi, R., Valiani, A., *et al.*, 2020a. Three-dimensional printing constructs based on the chitosan for tissue regeneration: State of the art, developing directions and prospect trends. *Materials* 13 (11), 2663.
- Pahlevanzadeh, F., Mokhtari, H., Bakhsheshi-Rad, H.R., *et al.*, 2020b. Recent trends in three-dimensional bioinks based on alginate for biomedical applications. *Materials* 13 (18), 3980.
- Parandoush, P., Lin, D., 2017. A review on additive manufacturing of polymer-fiber composites. *Composite Structures* 182, 36–53.
- Parham, S., Kharazi, A.Z., Bakhsheshi-Rad, H.R., *et al.*, 2020. Electrospun nano-fibers for biomedical and tissue engineering applications: A comprehensive review. *Materials* 13, 2153.
- Pranzo, D., Larizza, P., Filippini, D., Percoco, G., 2018. Extrusion-based 3D printing of microfluidic devices for chemical and biomedical applications: A topical review. *Micromachines* 9 (8), 374.
- Prashantha, K., Roger, F., 2017. Multifunctional properties of 3D printed poly (lactic acid)/graphene nanocomposites by fused deposition modeling. *Journal of Macromolecular Science, Part A* 54 (1), 24–29.
- Qiao, H., Zhang, Y., Huang, Z., *et al.*, 2018. 3D printing individualized triboelectric nanogenerator with macro-pattern. *Nano Energy* 50, 126–132.
- Qu, H., 2020. Additive manufacturing for bone tissue engineering scaffolds. *Materials Today Communications* 24, 101024.
- Reis, N., Ainsley, C., Derby, B., 2005. Viscosity and acoustic behavior of ceramic suspensions optimized for phase-change ink-jet printing. *Journal of the American Ceramic Society* 88 (4), 802–808.
- Rogina, A., Pribolšan, L., Hanžek, A., *et al.*, 2016. Macroporous poly (lactic acid) construct supporting the osteoinductive porous chitosan-based hydrogel for bone tissue engineering. *Polymer* 98, 172–181.
- Saari, M., Cox, B., Richer, E., Krueger, P.S., Cohen, A.L., 2015. Fiber encapsulation additive manufacturing: an enabling technology for 3D printing of electromechanical devices and robotic components. *3D Printing and Additive Manufacturing* 2 (1), 32–39.
- Sachs, E., Cima, M., Cornie, J., 1990. Three-dimensional printing: Rapid tooling and prototypes directly from a CAD model. *CIRP Annals* 39 (1), 201–204.
- Saengchairat, N., Tran, T., Chua, C.K., 2017. A review: Additive manufacturing for active electronic components. *Virtual and Physical Prototyping* 12 (1), 31–46.
- Sahranavard, M., Zamanian, A., Ghorbani, F., Shahrezaee, M.H., 2020. A critical review on three dimensional-printed chitosan hydrogels for development of tissue engineering. *Bioprinting* 17, e00063.
- Sarola, J., Wang, Y., Wei, Q., *et al.*, 2020. A review on 3D printed matrix polymer composites: Its potential and future challenges. *The International Journal of Advanced Manufacturing Technology* 106 (5–6), 1695–1721.
- Seerden, K.A., Reis, N., Evans, J.R., *et al.*, 2001. Ink-jet printing of wax-based alumina suspensions. *Journal of the American Ceramic Society* 84 (11), 2514–2520.
- Senatov, F.S., Niaza, K.V., Stepashkin, A.A., Kaloshkin, S.D., 2016. Low-cycle fatigue behavior of 3d-printed PLA-based porous scaffolds. *Composites Part B: Engineering* 97, 193–200.
- Sengupta, R., Bhattacharya, M., Bandyopadhyay, S., Bhowmick, A.K., 2011. A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites. *Progress in Polymer Science* 36 (5), 638–670.
- Serra, T., Planell, J.A., Navarro, M., 2013. High-resolution PLA-based composite scaffolds via 3-D printing technology. *Acta Biomaterialia* 9 (3), 5521–5530.
- Shofner, M.L., Lozano, K., Rodríguez-Macías, F.J., Barrera, E.V., 2003. Nanofiber-reinforced polymers prepared by fused deposition modeling. *Journal of Applied Polymer Science* 89 (11), 3081–3090.
- Singh, S., Ramakrishna, S., 2017. Biomedical applications of additive manufacturing: Present and future. *Current Opinion in Biomedical Engineering* 2, 105–115.
- Singh, S., Singh, G., Prakash, C., Ramakrishna, S., 2020. Current status and future directions of fused filament fabrication. *Journal of Manufacturing Processes* 55, 288–306.
- Takezawa, A., Kobashi, M., 2017. Design methodology for porous composites with tunable thermal expansion produced by multi-material topology optimization and additive manufacturing. *Composites Part B: Engineering* 131, 21–29.
- Tanwilaisiri, A., Xu, Y., Zhang, R., *et al.*, 2018. Design and fabrication of modular supercapacitors using 3D printing. *Journal of Energy Storage* 16, 1–7.
- Thomas, D.S., Gilbert, S.W., 2014. Costs and cost effectiveness of additive manufacturing. *NIST Special Publication* 1176, p. 12.
- Too, M.H., Leong, K.F., Chua, C.K., *et al.*, 2002. Investigation of 3D non-random porous structures by fused deposition modelling. *The International Journal of Advanced Manufacturing Technology* 19 (3), 217–223.
- Utela, B., Storti, D., Anderson, R., Ganter, M., 2008. A review of process development steps for new material systems in three dimensional printing (3DP). *Journal of Manufacturing Processes* 10 (2), 96–104.
- Vaezi, M., Seitz, H., Yang, S., 2013. A review on 3D micro-additive manufacturing technologies. *The International Journal of Advanced Manufacturing Technology* 67 (5–8), 1721–1754.
- Van Der Klift, F., Koga, Y., Todoroki, A., *et al.*, 2016. 3D printing of continuous carbon fibre reinforced thermo-plastic (CFRTP) tensile test specimens. *Open Journal of Composite Materials* 6 (01), 18.
- Wang, X., Jiang, M., Zhou, Z., Gou, J., Hui, D., 2017. 3D printing of polymer matrix composites: A review and prospective. *Composites Part B: Engineering* 110, 442–458.
- Wang, X.F., Lu, P.J., Song, Y., *et al.*, 2016. Nano hydroxyapatite particles promote osteogenesis in a three-dimensional bio-printing construct consisting of alginate/gelatin/hASCs. *RSC Advances* 6 (8), 6832–6842.
- Wang, Y., Lei, M., Wei, Q., *et al.*, 2020. 3D printing biocompatible L-Arg/GNPs/PLA nanocomposites with enhanced mechanical property and thermal stability. *Journal of Materials Science* 55 (12), 5064–5078.
- Wei, X., Li, D., Jiang, W., *et al.*, 2015. 3D printable graphene composite. *Scientific Reports* 5, 11181.
- Weng, Z., Wang, J., Senthil, T., Wu, L., 2016. Mechanical and thermal properties of ABS/montmorillonite nanocomposites for fused deposition modeling 3D printing. *Materials & Design* 102, 276–283.
- Wenz, A., Borchers, K., Tovar, G.E., Kluger, P.J., 2017. Bone matrix production in hydroxyapatite-modified hydrogels suitable for bone bioprinting. *Biofabrication* 9 (4), 044103.

- Wu, H., Fahy, W.P., Kim, S., *et al.*, 2020. Recent developments in polymers/polymer nanocomposites for additive manufacturing. *Progress in Materials Science* 111, 100638.
- Xiong, S., Zhang, X., Lu, P., *et al.*, 2017. A gelatin-sulfonated silk composite scaffold based on 3D printing technology enhances skin regeneration by stimulating epidermal growth and dermal neovascularization. *Scientific Reports* 7 (1), 1–12.
- Yamamoto, B.E., Trimble, A.Z., Minei, B., Ghasemi Nejhad, M.N., 2019. Development of multifunctional nanocomposites with 3-D printing additive manufacturing and low graphene loading. *Journal of Thermoplastic Composite Materials* 32 (3), 383–408.
- Yan, X., Gu, J., Zheng, G., *et al.*, 2016. Lowly loaded carbon nanotubes induced high electrical conductivity and giant magnetoresistance in ethylene/1-octene copolymers. *Polymer* 103, 315–327.
- Yildirim, E.D., Yin, X., Nair, K., Sun, W., 2008. Fabrication, characterization, and biocompatibility of single-walled carbon nanotube-reinforced alginate composite scaffolds manufactured using freeform fabrication technique. *Journal of Biomedical Materials Research Part B: Applied Biomaterials: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials* 87 (2), 406–414.
- Yoo, J., Cima, M.J., Khanuja, S., Sachs, E.M., 1993. Structural ceramic components by 3D printing. In: *Proceedings of the International Solid Freeform Fabrication Symposium* (1993).
- Yugang, D., Yuan, Z., Yiping, T., Dichen, L., 2011. Nano-TiO₂-modified photosensitive resin for RP. *Rapid Prototyping Journal* 17 (4).
- Zhang, B., Xie, C., Hu, J., Wang, H., Gui, Y., 2006. Novel 1–3 metal nanoparticle/polymer composites induced by hybrid external fields. *Composites Science and Technology* 66 (11–12), 1558–1563.
- Zhang, H., Mao, X., Du, Z., *et al.*, 2016. Three dimensional printed macroporous polylactic acid/hydroxyapatite composite scaffolds for promoting bone formation in a critical-size rat calvarial defect model. *Science and Technology of Advanced Materials* 17 (1), 136–148.
- Zheng, H., Zhang, J., Lu, S., Wang, G., Xu, Z., 2006. Effect of core-shell composite particles on the sintering behavior and properties of nano-Al₂O₃/polystyrene composite prepared by SLS. *Materials Letters* 60 (9–10), 1219–1223.
- Zhong, W., Li, F., Zhang, Z., Song, L., Li, Z., 2001. Short fiber reinforced composites for fused deposition modeling. *Materials Science and Engineering: A* 301 (2), 125–130.
- Ziaee, M., Crane, N.B., 2019. Binder jetting: A review of process materials, and methods. *Additive Manufacturing* 28, 781–801.

New Design Consideration of Polymer Matrix Composite Materials

Peng Liu, Lanzhou University, Lanzhou, China

© 2021 Elsevier Inc. All rights reserved.

Introduction

In the last decades, the polymer matrix composite materials have attracted more and more interests in various potential applications, by improving the mechanical and thermal property by introducing the inorganic nanomaterials as reinforcement agents, or providing special functions (such as magnetic, electrical or electrochemical property) with functional inorganic nanomaterials. The physical blending approach is the most used method to prepare the polymer matrix composite materials, also the simplest one, in which the fillers were surface modified with small organic molecules to reduce surface polarity or improve the interfacial property between the polymeric matrices. For the inorganic nanomaterials, which show nanoscale size and strong surface polarity, they might transfer through the polymeric matrices and form aggregates in service (Fig. 1), especially for the applications at a high temperature near to the glass transition temperature (T_g) of the polymeric matrices (Colonna *et al.*, 2014).

In fact, besides the annealing treatment (Liu *et al.*, 2015b) and the thermal conduction application or those at elevated temperatures (Lewin *et al.*, 2006), it usually produces heat in some applications, such as periodic bending, shocking or vibration (Shabaniverki *et al.*, 2018), electric conduction (Ren *et al.*, 2018), tribology (Massod *et al.*, 2017; Zhao *et al.*, 2016), irradiation (Asadinezhad *et al.*, 2013; Patel *et al.*, 2006) and so on. In such cases, the temperature will rise because of the transformation of the impact energy, electric energy, mechanical energy or radiant energy into heat energy. The flame-retardant performance could be enhanced by the migration of the clay mineral or SiO_2 particles to surface of nanocomposites, which reinforce the intumescent char (Kiliaris and Papaspyrides, 2010; Laoutid *et al.*, 2009; Zhang *et al.*, 2017). It has been paid much attention for the safety in the food packaging application (Bandyopadhyay and Ray, 2019; Farhoodi, 2016).

The miscibility and migration of the inorganic nanomaterials in the polymeric matrices has been rarely involved in most of the reported works except for the food packaging application, because that the structure and performance of the as-prepared composites were usually analyzed, but not in service or after service. However, the phenomenon would lead to poor stability of material properties. The question is usually of no great importance in the crystalline polymer matrices, because that the inorganic nanomaterials could be inlaid in the continuous phase formed by the polymer crystals. The migration of the inorganic nanomaterials could not be avoided even in the hydrogels and vulcanized rubbers with low crosslinking degree.

In recent years, the polymer matrix nanocomposite materials have been designed with the functionalized inorganic nanomaterials as crosslinking agents. In the designed structure, the inorganic nanomaterials were introduced into the 3-D covalently crosslinked networks in the resultant nanocomposite materials. Therefore, the migration of the inorganic nanomaterials could be efficiently avoided, and the stable miscibility of the inorganic nanomaterials could be achieved in the advanced composite materials. Such 3-D covalently crosslinked networks could be easily prepared via the in-situ polymerization in presence of the functionalized inorganic nanomaterials (Liu *et al.*, 2014d; Zhu *et al.*, 2016a) or the surface modification (Pan and Liu, 2018), which showed negative effect on the processing and molding of the resultant nanocomposite materials. For ease of processing and application, the advanced composite materials with inorganic nanomaterials in their 3-D covalently crosslinked networks were usually synthesized with a one-step for direct application, or two-step method in which the crosslinked networks were formed with the functionalized inorganic nanomaterials during the processing and molding (Bakir *et al.*, 2020). In the present article, the design and application progress in the advanced composite materials is reviewed, classified in their applications, with emphasis on the structure-performance relationship. Additionally, the future development direction of this field was also prospected in the last.

General Research

The 3-D covalently crosslinked networks have been widely fabricated via the crosslinking during molding approach, with the inorganic nanomaterials as crosslinkers (Fig. 2), mainly the carbon nanomaterials and SiO_x nanoparticles, respectively.

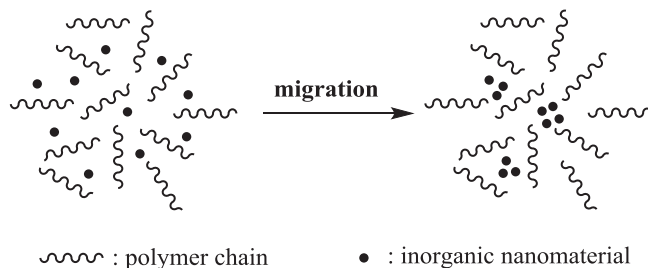


Fig. 1 Aggregation of the inorganic nanomaterials in the polymeric matrix via migration.

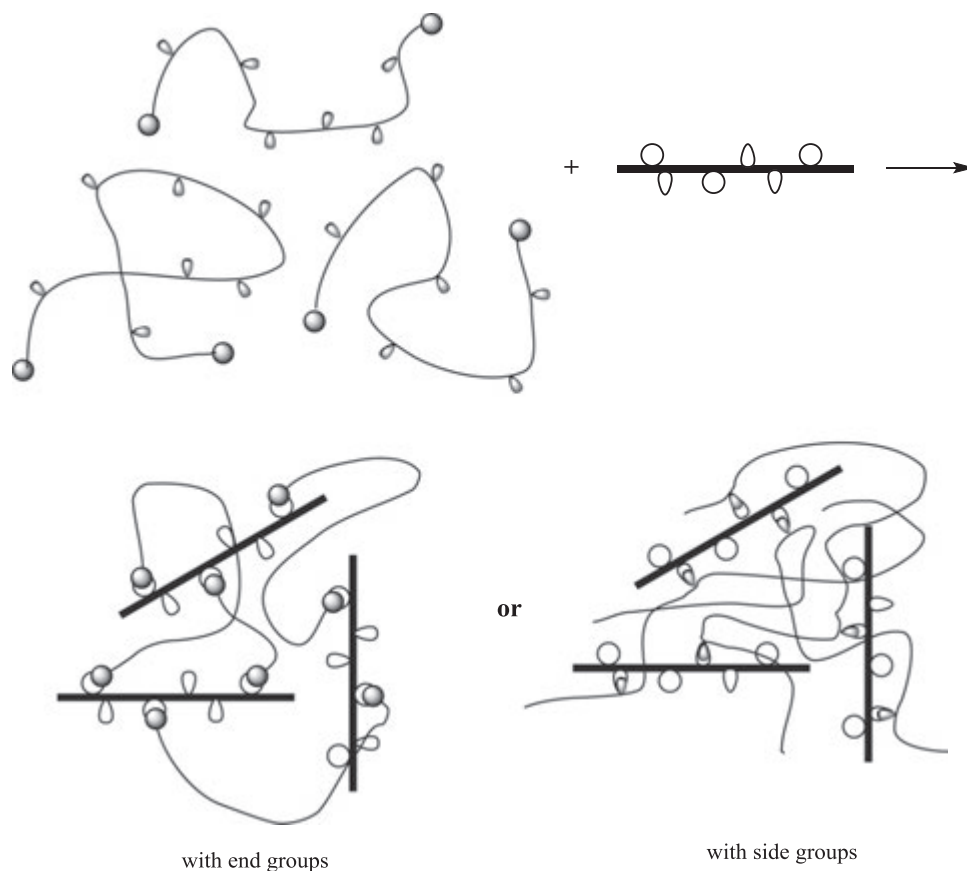


Fig. 2 Crosslinking of polymer matrices with multifunctional inorganic nanomaterials with the end groups or side groups in polymer chains.

Carbon Nanomaterials

Carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene, have been widely used in polymer matrix nanocomposite materials, because of their excellent mechanical strength, as well as high thermal and electrical conductivity. They were usually used after exfoliation, in which they were oxidized to improve their aqueous dispersibility. During the oxidization, oxygen-containing functional groups could be introduced, facilitating the application as multifunctional crosslinkers.

Carbon nanotubes

The carboxyl groups in the oxidized CNTs could act directly the functional groups for the crosslinking. For example, mechanically robust single-walled carbon nanotubes (SWCNTs)/poly(allylamine) composites were designed by crosslinking the polymer with carboxylic acid functionalised SWCNTs (Satti *et al.*, 2010). The ultimate tensile strength and Young's modulus of the crosslinked buckypaper films were 42 MPa and 11 GPa respectively, more than 9 times higher than the one for noncrosslinked PAH infiltrated buckypaper films.

Besides, the amino functionalised CNTs could be synthesized by the functional group conversion reaction for other polymer matrices (Fan *et al.*, 2018; Zhu *et al.*, 2019). Similar as the above buckypaper films, the crosslinked aerogels were obtained in the two works, because of the release of small molecules in the condensation.

Additionally, the multiwalled carbon nanotubes (MWCNTs) were functionalized with epoxy prepolymer to introduce epoxy groups. Then they were used as crosslinker for the waterborne polyurethane (WPU) (Wang *et al.*, 2020). The composite films were formed by the reaction of the epoxy groups in MWCNTs and the carboxyl or amino groups in the WPU chains, showing a significant improvement in the mechanical property, thermal stability, water resistance, and electrical conductivity.

Graphene

Graphene oxide (GO) nanosheets, which could be obtained by the oxidation and exfoliation of graphite, possess plentiful functional groups such as hydroxyl, epoxide and carboxyl ones. Such functional groups could be used for the crosslinking of various polymer matrices (Ha and Ellison, 2018). They could also be transformed into epoxide (Shen *et al.*, 2013), amino (Nonahal *et al.*, 2018), vinyl (Vesile *et al.*, 2019) and thiol groups (Luo *et al.*, 2016) for different polymer matrices.

As another candidate, GO could generate free radicals upon heating, enabling covalent crosslinking of styrene-butadiene rubber (SBR) (Xing *et al.*, 2017), allowing better mechanical properties than SBR crosslinked with conventional sulfur or dicumyl peroxide.

Other carbon nanomaterials

Well-crosslinked polybenzoxazine (PBz) networks were designed by the condensation of benzoxazine in presence of amine-functionalized carbon balls (CBs-NH₂) (Periyasamy *et al.*, 2020). The thermal and mechanical properties of the nanocomposites (PBz/CBs-NH₂) were found to be outstanding compared with those of the neat PBz.

POSS and Silica Nanoparticles

Polyhedral oligomeric silsesquioxane (POSS), cube-octameric framework with an inorganic core of about 0.5 nm, has attracted intense interests for the crosslinked nanocomposites, owing to the eight organic corner functional groups. Thiol-modified POSS (POSS-SH) has been used as crosslinker for poly(styrene-*b*-butadiene-*b*-styrene) (SBS) via the thiol-ene reaction (Bai *et al.*, 2014). With 1% POSS-SH, the maximum of stress at break of 23.4 MPa and elongation at break of about 1000% were achieved, distinctly different from the conventional inorganic filler reinforced elastomer where the increase of stress was usually sacrificed by the decrease of elongation. It has been explained that the SBS changed from the circle inland structures to lamella structures in the resultant elastomers.

Low density polyethylene (LDPE) has been crosslinked with the octavinyl polyhedral oligomeric silsesquioxane (OVPOSS) as crosslinker, in presence of dicumyl peroxide (DCP) as initiator for the radical reaction (Wu *et al.*, 2014). The storage modulus increased while the thickness of the lamellar crystal of polyethylene decreased because of the restricted chain mobility and folding to form crystal domain. The OVPOSS has also been used for the photo-crosslinking of poly(propylene fumarate), showing distinct physical properties and promoted MC3T3 cell functions (Wang *et al.*, 2011).

To improve the ablation resistance, hydroxyl-terminated polydimethylsiloxane was crosslinked with multi-ethoxy POSS at room temperature (Liu *et al.*, 2020a). Besides the strengthened mechanical strength, the thermal stability and heat shielding properties of composite were also enhanced, owing to the effective crosslinking with the uniformly dispersed POSS. The cross-linked hybrid composites have also designed with the multimethacryloxy- (Przadka *et al.*, 2015), methacrylate- or thiol- (Ito *et al.*, 2014), or octa(3-azidopropyl)- (Zhang *et al.*, 2020a) substituted POSS.

The hydrolysis-condensation approach seems a simple method to fabricate the crosslinked composites with in situ generated silica particles as crosslinker. However, because of the release of small molecules during the sol-gel process, it could only be used for the fabrication of hybrid thin films. For example, Polydimethyldiphenylsiloxanes/silica interconnected networks were designed by the reaction between the polydimethyldiphenylsiloxane- α,ω -diols and tetraethoxysilane (TEOS) (Cazacu *et al.*, 2010). With a high silica content, the enhanced thermal stability was achieved without crystallization because of the in the dense silica network.

Other Nanomaterials

γ -Methacryloxypropyltrimethoxysilane (MPTS) modified nanoclays (Liu *et al.*, 2014d; Zhu *et al.*, 2016a) and TiO₂ nanotubes (Villenas *et al.*, 2015) have been also used as multifunctional crosslinkers in the in-situ polymerization of vinyl-based monomers. The higher Vickers microhardness and better thermal stability were achieved owing to the gelation, although it might decrease the processability of the resultant nanocomposites.

Carbon nanotubes-silica (CNTs-SiO₂) nanohybrids have also been designed as multifunctional crosslinkers for the solution styrene butadiene rubber (*s*-SBR), via surface modification with MPTS (Wang *et al.*, 2013). The nanohybrids accelerated the vulcanization process and improved the crosslinking degree of vulcanizates. With 10 phr (parts per hundred of rubber), The tensile moduli at 100% elongation (M100) and tensile strength had 54% and 28% increase, respectively. Largely enhanced storage modulus and slightly increased thermal conductivity were also obtained for the resultant vulcanizates.

Compared with the crosslinking via the condensation reaction which could only be used for the fabrication of crosslinked aerogels, coatings or films, the crosslinking via the ring-opening reaction of epoxide and thiol-ene click reaction show promising potential, owing to the addition reaction characteristics.

Functional Materials

Adsorbents and Hydrogels for Biomedical Applications

Inorganic nanomaterials have been widely incorporated into the adsorbents and hydrogels to enhance the strength of polymer matrices. The inorganic nanomaterials, which were encapsulated or conjugated into the crosslinked polymeric networks, played an important role in the formation of the porous structure of the nanocomposite adsorbents and hydrogels, subsequently possessing obvious effect on the swelling and adsorption behaviors.

Chen, Xiong and Peng *et al* designed poly(N-isopropylacrylamide-co-dimethylaminoethyl methacrylate) hydrogels co-crosslinked with both organic crosslinker and inorganic crosslinker, N,N'-methylenebis(acrylamide) and OVPOSS, respectively (Chen *et al.*, 2013). Due to the microphase separation, the interconnected micropores were produced, endowing a faster deswelling rate.

The composite hydrogels could be synthesized by the crosslinking of the ready-made polymers with functional nanomaterials as crosslinkers. For examples, polymer hybrid hydrogels were synthesized by mixing a water-soluble polymer with trimethoxysilyl side groups with silica nanoparticles (Takafuji *et al.*, 2011). Besides, amphiphilic composite nanoparticles were designed by the reaction of

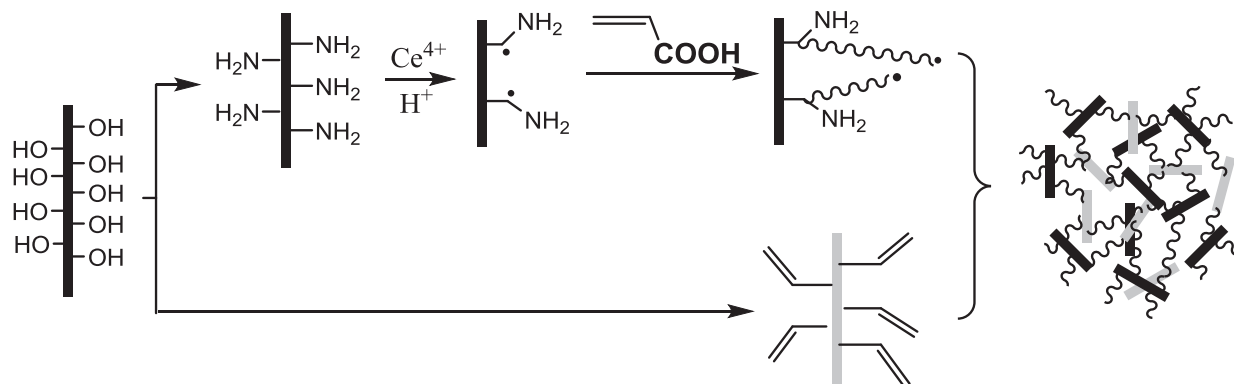


Fig. 3 Nanocomposite hydrogels with functionalized attapulgite nanorods as initiator and crosslinker respectively.

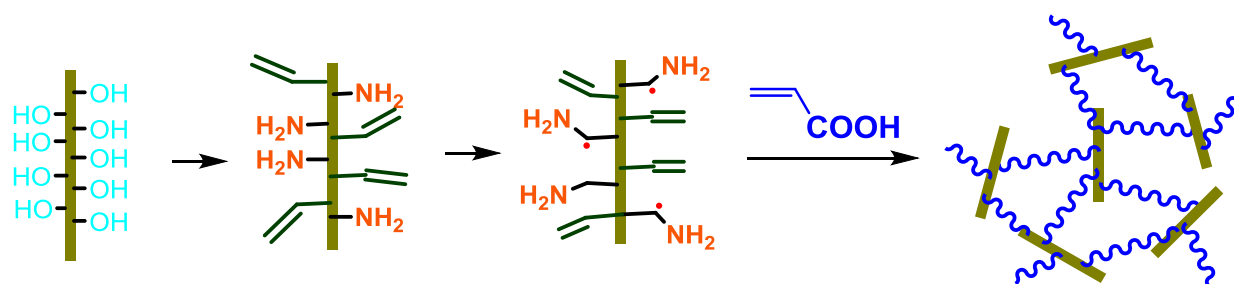


Fig. 4 Nanocomposite hydrogels with bi-functionalized attapulgite nanorods.

the urethane acrylate modified silica nanoparticles with amphiphilic reactive oligomers, in which the silica nanoparticles were chemically connected with each other through the hydrophobic crosslinked chains (Kim *et al.*, 2011). The obtained amphiphilic composite nanoparticles could be easily dispersed into water owing to their surface hydrophilic brushes. They showed high adsorption capacity toward hydrophobic molecules, and 100% of retention recovery and higher permeate flux in the ultrafiltration application.

The in-situ polymerization approach might be the promising method to fabricate nanocomposite hydrogels. Thermo-responsive hydrogels have been designed with enhanced mechanical properties, by the in-situ radical polymerization of N-isopropylacrylamide (NIPAM) and acrylamide (AAM) with vinyltriethoxysilane (VTES) modified GO as crosslinker (Wang *et al.*, 2017). The attapulgite-based initiator and crosslinker separately (Fig. 3) (Zhu *et al.*, 2014) or simultaneously (Fig. 4) (Zhu *et al.*, 2016b) have also been designed for crosslinked nanocomposite hydrogel via the in-situ radical polymerization.

Liu and co-workers designed attapulgite-based nanocomposite hydrogels with excellent reusability for selective adsorption of heavy metal ions via an “one-pot” inverse suspension polymerization, in which the attapulgite and the magnetic nanoparticles were surface-modified with polymerable groups as unique crosslinkers (Jiang and Liu, 2014a,b,c; Jiang *et al.*, 2015; Liu *et al.*, 2014a,b,c, 2015a). These nanocomposite hydrogel adsorbents showed outstanding anti-pressure resistance and the anti-shearing ability, without broken by loading a pressure of 3 kg as well as stirring for 2 h at 5000 rpm.

Hydroxyapatite nanorods and nanowires have been modified with acrylate groups to photo-crosslink methacrylated gelatin (GelMA) into gelatin cryogels (Cu *et al.*, 2020). The proposed composite cryogels showed promising potential as bone repairing materials, owing to excellent performances such as high porosity, appropriate water retention, shape recovery, and fast resilience features, as well as good biocompatibility and cell affinity.

Highly stretchable nanocomposite hydrogel has been fabricated via in-situ free radical polymerization of acrylamide with exfoliated two-dimensional MXene (Ti_3C_2) nanosheet as crosslinker (Zhang *et al.*, 2020b). The honeycomb-like fine structure with uniform pores were formed and attributed to the enhanced mechanical and drug release behaviors.

Shape Memory and Self-Healing Materials

Polyurethane (PU) has been widely used as the polymer matrix for the shape memory and self-healing composite materials. Electroactive shape memory polyurethane composite has been designed by in-situ crosslinking polymerization of HO-PCL-OH, 4,4'-methylene bis(phenylisocyanate) (MDI), and 1,4-butanediol (BD), in presence of hydroxyl modified MWCNTs (Jung *et al.*, 2010). The resultant composites possessed shape retention of 92% and shape recovery of 95%, respectively. Furthermore, the surface temperature and the shape recovery in applied electric voltage were strongly influenced by the dispersed structure of the MWCNTs in the obtained composites. Compared with the MWCNTs-based composites, the graphene-based one, which was also

synthesized with the similar method as above, showed higher modulus and breaking stress, and exceptional elongation-at-break. The resulting composite exhibited 97% shape recovery, 95% shape retention, enhanced shape recovery force, and fast electroactive shape recovery rate (Rana *et al.*, 2013).

Lee and Kim developed a novel method to fabricate the shape memory GO/PU composite, by UV curing the acrylate-terminated PU with allyl isocyanate modified GO (Lee and Kim, 2013). The glassy and rubbery state moduli, yield strength, T_g , shape fixity and shape recovery ratios were increased on adding up to 1.0 wt% loading. At higher concentrations, graphene is vulnerable to aggregation and auto-inhibition.

Biodegradable magnetic-sensitive shape memory Fe_3O_4 /poly(ϵ -caprolactone) (PCL) nanocomposites were designed via the photo-crosslinking of the vinyl-terminated PCL prepolymer with γ -(methacryloyloxy) propyl trimethoxy silane (KH570) modified Fe_3O_4 nanoparticles (Gao *et al.*, 2018). The nanocomposites possessed superior mechanical properties and excellent shape memory properties in both hot water and an alternating magnetic field.

The self-healing composite materials were mainly designed via the Diels–Alder (DA) reaction. Covalently bonded graphene oxide/polyurethane (GO/PU) composites with significant reinforcement and thermally healable properties were developed via in situ polymerization based on the DA reaction of bifunctional maleimide and the PU prepolymer, which was prepared with GO, MDI, and poly(tetramethylene glycol) and blocked by using furfuryl alcohol (FA) (Li *et al.*, 2014). With 0.1 wt% of GO, the tensile modulus of GO/PU composites increased from 9.80 MPa to 21.95 MPa, and the tensile strength and elongation at break of the GO/PU composites increased by more than 367% and 210% respectively, with a high healing efficiency of 78%. The similar self-healing GO/PU composite materials have also been designed with isocyanate modified reduced GO, and N-(2,3-dihydroxypropyl)-maleimide and furan-terminated hexamethylene diisocyanate trimer as chain extender and crosslinking reagent respectively (Du *et al.*, 2020), or maleimide modified GO and furan- and maleimide-contained linear PU polymers (Lin *et al.*, 2017).

Handique and Dolui designed a dual functionalized self-healing epoxy composite by forming the reversible crosslinked structure via the DA reaction between furfuryl grafted epoxy prepolymer, furfuryl modified MWCNTs and bifunctional maleimide (Handique and Dolui, 2019). The proposed epoxy composite possessed not only enhanced mechanical properties but also thermal remendability that enabled elimination of cracks, due to the successive retro-DA and DA reactions, which led to crack healing upto 79.82% healing efficiency in a controlled manner through chain reconnection.

The self-healing TiO_2 /polyimine composite has been fabricated by the reaction of the amino-functionalized TiO_2 microspheres with diethylenetriamine and terephthalaldehyde (Lv *et al.*, 2018). With optimized fillers amount of 3%, the tensile strength and modulus of the composite were enhanced by 14% and 97%, respectively, and tensile toughness is maintained at 4.3 ± 0.86 , which is the same with polyimine. Furthermore, the self-healing property was also achieved via the solvent-involved curing process.

Electrochemical Applications

Owing to the excellent dimensional and chemical stabilities of the novel crosslinked composite materials, they have been widely used as membrane in electrochemical fields, especially as the proton-exchange membranes for direct methanol fuel cells (DMFCs). For the special application, the sulfonated poly (arylene ether ketone) (SPAEC) has been mainly used as the polymer matrix, with the help of sol-gel technology. The hybrid proton-exchange membranes have been designed by the crosslinking of SPAEC with pendant propenyl moiety via radical process in presence of vinyl-functionalized silica (Feng *et al.*, 2010). With a silica content of 8%, the methanol permeability coefficient was $6.02 \times 10^{-7} \text{ cm}^2/\text{s}$, a 2.64-fold decrease compared with that of the pristine SPAES membrane. Chemically stable hybrid polymer electrolyte membranes have been designed by a combination of silane-crosslinking and thiol-ene click chemistry based on SPAEC as a proton exchange membrane for direct methanol fuel cell applications (Gao *et al.*, 2012). It was found that the Si-O-Si cross-linked structure makes a great contribution to the improvement of dimensional and oxidative stabilities. By using two functional silanes, 3-glycidoxypropyl-trimethoxysilane and 3-mercaptopropyl-trimethoxysilane in the silane-crosslinking, the proton conductivity of the hybrid membrane was 0.20 S/cm at 80°C (Lin *et al.*, 2011).

Sulfonated polyimide (SPI)- SiO_2 hybrid proton-exchange membranes have been designed by the co-hydrolysis and condensation of 3-glycidoxypropyltrimethoxysilane and TEOS in presence of amino-terminated SPI prepolymers (Liu *et al.*, 2010). The introduction of SiO_2 improved the methanol resistance while retaining good proton conductivity. With 30% of SiO_2 , the membrane possessed a proton conductivity of 10.57 mS/cm at 80°C and methanol permeability of $2.3 \times 10^{-6} \text{ cm}^2/\text{s}$ possibly because the crosslinking structure and SiO_2 phases formed in the hybrids could retain water and were helpful to proton transport.

Crosslinked poly(ethylene glycol) (PEG)/sulfonated polyhedral oligosilsesquioxane (sPOSS) hybrid membranes have been fabricated with poly(ethylene glycol) (PEG) and sulfonated polyhedral oligomeric silsesquioxane (POSS-SO₃H) with urethane crosslinks (Chang and Shin, 2011). The proton conductivity increased while the methanol permeability decreased with increasing POSS content in the hybrid membrane. The proposed hybrid membranes demonstrated proton conductivities comparable to that of Nafion 117 while exhibiting lower methanol permeability as compared to Nafion 117.

Crosslinked sulfonated poly(vinyl alcohol)/sulfonated MWCNTs nanocomposite membranes have been designed by facile crosslinking of sulfonated poly(vinyl alcohol) with sulfonated MWCNTs (Yun *et al.*, 2011). The composite membranes exhibited excellent proton conductivity ranging from 0.032 to 0.075 S/cm as well as low methanol permeability ranging from 1.12×10^{-8} to $3.32 \times 10^{-9} \text{ cm}^2/\text{s}$ at 60°C.

Graphene-based hybrid membrane has been fabricated by crosslinking the 4-chlorostyrene functionalized GO with sulfonated polysulfone (Yang *et al.*, 2018). It possessed a high proton conductivity of 0.462 S/cm at 90°C under hydrated conditions, with a low methanol permeability of $1.71 \times 10^{-6} \text{ cm}^2/\text{s}$ at 30°C.

Polybenzimidazole (PBI-OO) based composite membranes have been designed for the high temperature proton exchange membrane fuel cell (HT-PEMFC) application, by thermal curing of polybenzimidazole (PBI-OO) with the sulfophenylated TiO_2 particles (Krishnan *et al.*, 2018). It showed the highest uptake of 392% and a proton conductivity of 98 mS/cm at 160°C.

Miao *et al.* (2018) developed a mussel-inspired strategy to fabricate the rGO-based anion exchange membranes, by crosslinking the quaternized polysulfone (QPSU) with polydopamine-functionalized rGO. With 1.5% addition of the functionalized rGO, the membrane possessed 57% improvement in the hydroxide conductivity than that of pure QPSU membrane and reached the highest value of 61 mS/cm at 80°C. Furthermore, the crosslinked membranes exhibited strong dimensional stability, good mechanical strength, comparable alkaline stability and improved methanol permeability.

Novel gel polymer electrolyte has been designed for the rechargeable lithium batteries, by crosslinking the epoxycyclohexyl POSS with amine-terminated butadiene-acrylonitrile copolymer (Li *et al.*, 2012). It exhibited ionic conductivity of 2.0×10^{-4} S/cm at 30°C and good electrochemical stability to 4 V from cyclic voltammogram tests.

Functional Coatings

Waterborne polyurethane (WPU)/polyphenylsilsequioxanes (PPSQ) coating films were designed by the in-situ sol-gel reaction between phenyltrimethoxysilane and the alkoxy silane side-groups in WPU during film formation (Li *et al.*, 2018). The proposed method could efficiently avoid the phase separation in composite films prepared by physical blending, by forming more homogeneous crosslinking structures in the polymer matrix. Owing to hybrid networks with confined phase separation scales, the enhanced modulus, tensile strength and thermal stability were achieved with decreased water absorption.

Epoxy hybrid composites have been fabricated by curing brominated epoxy resin with octaaminophenyl POSS (Chen *et al.*, 2012). With 1% of octaaminophenyl POSS, the thermal and mechanical properties of the composites were enhanced while the water absorption declined significantly. Besides, the dielectric constant was 0.5 less than that of the epoxy resin in the range of 100 Hz–40 MHz.

Facing the conflict between dielectric constant and breakdown strength in the high-temperature ceramic/polymer nanocomposites for energy storage applications, a new strategy has been established to simultaneously improve breakdown strength and discharged energy density by a step-by-step, controllable dual crosslinking process, in which a strengthened interface was constructed between the heatresistant poly(arylene ether sulfone)s (DPAES) and BaTiO_3 nanoparticles with bisbenzocyclobutene groups to reduce molecular chains relaxation under elevated temperatures (Liu *et al.*, 2020b). The dual crosslinking procedures were controllable via tuning temperature and time of the chemical reaction: i) the polymer chains crosslinked to the surface-treated inorganic fillers at a lower temperature, which can strengthen the interfacial interaction at the organic–inorganic interface, inhibiting the formation of interfacial defects and limiting the local molecular changes motion in the same time; and ii) the rest polymeric matrix were crosslinked at a higher temperature which can further limit molecular chains motion in the majority part of the composite matrix. The proposed strategy is expected as a promising avenue for compact, flexible, and high thermal stable high energy capacitive energy storage devices at relatively high temperatures.

WPU-based anticorrosive coatings have been developed by curing the WPU molecules with polycarbodiimide modified GO (Cui *et al.*, 2020). The superior anticorrosive properties benefited from the barrier properties of well-dispersed graphene layers, the crosslinking structure along the functionalized graphene/WPU interfaces, as well as the improved water resistance of the coatings.

Thermally Conducting Polymer Materials

Thermally conductive MWCNTs/epoxy nanocomposites have been prepared by curing epoxy resin with different diamine-functionalized MWCNTs as both co-curing agents and conducting fillers (Choi *et al.*, 2017). With the same MWCNTs concentration, the crosslinking degree was affected by the diamines used. A high crosslinking density enhanced the thermal conductivity via phonon transport, but for high MWCNTs concentrations, a high crosslink density hindered the formation of a percolating network and lowered the thermal conductivity. The highest thermal conductivity of 0.283 W/mK was achieved with 3% of the octamethylenediamine modified MWCNTs.

The thermally conductive epoxy nanocomposites have also been designed with poly(glycidyl methacrylate)-grafted graphene as co-curing agent (Oh *et al.*, 2019). With a functional graphene content of 7%, the thermal conductivity reached 0.75 W/mK, meaning a thermal conductivity enhancement of 249%.

To balance the thermal conductivity and peel strength of the acrylic pressure-sensitive adhesive (PSA) with perspective for application in miniature electronic industries, bifunctional isocyanatoethylmethacrylate modified GO has been incorporated in the in-situ polymerization of acrylic monomers, followed with UV curing (Vu *et al.*, 2019). Within the range of filler content of – 3% and UV-radiation dosages of (400–3000) mJ/cm², the thermal conductivity and peel strength of the acrylic PSA-system under investigation varied in the range of 0.17–1.03 W/mK and 2831–299 g/25 mm.

Gas Barrier Membranes

Ha, Park, Ha, *et al.* developed a simple process for strong and flexible elastomer from a reactive mixture of GO and functional telechelic poly(dimethylsiloxane) (PDMS) (Ha *et al.*, 2016a). The resultant composite elastomers were highly crosslinked but highly flexible such that it can be stretched up to 300% of its original length. As a single gas barrier membrane, the gas permeability decreased 45% for N_2 , O_2 , CH_4 or CO_2 by incorporating 1% of GO, indicating its potential use in practical applications. Increasing the wt% amount of GO to 8%, the gas permeability decreased more than 99.9% (Ha *et al.*, 2016b).

Conclusion and Prospects

In summary, the reported works demonstrated that successful enhancement of the crosslinked polymer matrix composite materials with inorganic nanomaterials as crosslinking agents especially the mechanical and thermal properties, owing to the covalent crosslinking as well as the uniform dispersion of the inorganic nanomaterials. Furthermore, conductive carbon nanomaterials could also endow the electric and thermal conductivity, except the barrier function of layered graphene.

However, the release of small molecules in the condensation reaction is still a challenge in the crosslinking during molding approach, limiting its application for only crosslinked aerogels, coatings or thin films. The crosslinking via addition reaction should be a promising direction in the future research. Furthermore, the UV-irradiation crosslinking could only be used for the coatings or thin films, but not bulky materials. So the thermal-induced addition reaction might be the most practical technology to design and manufacture of the high-performance and low-cost polymer matrix composite materials for various applications, such as DA chemistry.

References

- Asadinezhad, A., Khonakdar, H.A., Jafri, S.H., *et al.*, 2013. A surface analysis of polypropylene/clay nanocomposites exposed to electron irradiation. *Journal of Applied Polymer Science* 128, 1569–1574.
- Bai, J., Shi, Z.X., Yin, J., *et al.*, 2014. A simple approach to preparation of polyhedral oligomeric silsesquioxane crosslinked poly(styrene-*b*-butadiene-*b*-styrene) elastomers with a unique micro-morphology via UV-induced thiol-ene reaction. *Polymer Chemistry* 5, 6761–6769.
- Bandyopadhyay, J., Ray, S.S., 2019. Are nanoclay-containing polymer composites safe for food packaging applications? – An overview. *Journal of Applied Polymer Science* 136, 47214.
- Bakir, M., Meyer, J.L., Pang, S.Y., *et al.*, 2020. Merging versatile polymer chemistry with multifunctional nanoparticles: An overview of crosslinkable aromatic polyester matrix nanocomposites. *Soft Matter* 16, 1389–1403.
- Cazacu, M., Vlad, A., Alexandru, M., *et al.*, 2010. Polydimethyldiphenylsiloxanes/silica interconnected networks: Preparation and properties evaluation. *Polymer Bulletin* 64, 421–434.
- Chang, Y.-W., Shin, G., 2011. Crosslinked poly(ethylene glycol) (PEG)/sulfonated polyhedral oligosilsesquioxane (sPOSS) hybrid membranes for direct methanol fuel cell applications. *Journal of Industrial and Engineering Chemistry* 17, 730–735.
- Chen, G.-X., Si, L.X., Lu, P., *et al.*, 2012. Epoxy hybrid composites cured with octaaminophenyl polyhedral oligomeric silsesquioxane. *Journal of Applied Polymer Science* 125, 3929–3935.
- Chen, Y., Xiong, Y.Q., Peng, C., *et al.*, 2013. Synthesis and characterization of polyhedral oligomeric silsesquioxane hybrid co-crosslinked poly(*N*-isopropylacrylamide-co-dimethylaminoethyl methacrylate) hydrogels. *Journal of Polymer Science, Part B: Polymer Physics* 51, 1494–1504.
- Choi, J.H., Song, H.J., Jung, J., *et al.*, 2017. Effect of crosslink density on thermal conductivity of epoxy/carbon nanotube nanocomposites. *Journal of Applied Polymer Science* 134, 44253.
- Colonna, S., Cuttica, F., Frache, A., 2014. Aging of EVA/organically modified clay: effect on dispersion, distribution and combustion behaviour. *Polymer Degradation and Stability* 107, 184–187.
- Cui, J.C., Xu, J.C., Li, J., *et al.*, 2020. A crosslinkable graphene oxide in waterborne polyurethane anticorrosive coatings: Experiments and simulation. *Composites Part B* 188, 107889.
- Du, W.N., Jin, Y., Shi, L.J., *et al.*, 2020. NIR-light-induced thermoset shape memory polyurethane composites with self-healing and recyclable functionalities. *Composites Part B* 195, 108092.
- Fan, W., Zuo, L.Z., Zhang, Y.F., *et al.*, 2018. Mechanically strong polyimide/carbon nanotube composite aerogels with controllable porous structure. *Composites Science and Technology* 156, 186–191.
- Farhoodi, M., 2016. Nanocomposite materials for food packaging applications: Characterization and safety evaluation. *Food Engineering Reviews* 8, 35–51.
- Feng, S.G., Shang, Y.M., Wang, Y.Z., *et al.*, 2010. Organic-inorganic crosslinked and hybrid membranes derived from sulfonated poly(arylene ether sulfone)/silica via sol-gel process. *Journal of Power Sources* 195, 2541–2548.
- Gao, S.S., Zhao, C.J., Na, H., 2012. Chemically stable hybrid polymer electrolyte membranes prepared by silane-crosslinking and thiol-ene click chemistry. *Journal of Power Sources* 214, 285–291.
- Gao, Y.L., Zhu, G.M., Xu, S.G., *et al.*, 2018. Biodegradable magnetic-sensitive shape memory poly(ϵ -caprolactone)/Fe₃O₄ nanocomposites. *Journal of Applied Polymer Science* 135, 45652.
- Gu, L.H., Zhang, Y.F., Zhang, L.W., *et al.*, 2020. Comparative study of gelatin cryogels reinforced with hydroxyapatites with different morphologies and interfacial bonding. *Biomedical Materials* 15, 035012.
- Ha, H., Ellison, C.J., 2018. Polymer/graphene oxide (GO) thermoset composites with GO as a crosslinker. *Korean Journal of Chemical Engineering* 35, 303–317.
- Ha, H., Park, J., Ha, K., *et al.*, 2016a. Synthesis and gas permeability of highly elastic poly(dimethylsiloxane)/graphene oxide composite elastomers using telechelic polymers. *Polymer* 93, 53–60.
- Ha, H., Park, J., Ando, S., *et al.*, 2016b. Gas permeation and selectivity of poly(dimethylsiloxane)/graphene oxide composite elastomer membranes. *Journal of Membrane Science* 518, 131–140.
- Handique, J., Dolui, S.K., 2019. A thermally remendable multiwalled carbon nanotube/epoxy composites via Diels-Alder bonding. *Journal of Polymer Research* 26, 163.
- Ito, M., Shimasaki, T., Teramoto, N., *et al.*, 2014. Photo-cured organic-inorganic hybrid composites of methacrylate-terminated 4-arm star-shaped ϵ -caprolactone oligomer and methacrylate- or thiol-substituted polysilsesquioxane. *Journal of Polymer Research* 21, 507.
- Jiang, L.P., Liu, P., 2014a. Novel magnetic fly ash/poly(acrylic acid) composite microgel for selective adsorption of Pb(II) ion: synthesis and evaluation. *Industrial & Engineering Chemistry Research* 53, 2924–2931.
- Jiang, L.P., Liu, P., 2014b. Design of magnetic attapulgit/fly ash/poly(acrylic acid) ternary nanocomposite hydrogels and performance evaluation as selective adsorbent for Pb²⁺ ion. *ACS Sustainable Chemistry & Engineering* 2, 1785–1794.
- Jiang, L.P., Liu, P., 2014c. Covalently crosslinked fly ash/poly(acrylic acid-co-acrylamide) composite microgels as novel magnetic selective adsorbent for Pb²⁺ ion. *Journal of Colloid and Interface Science* 426, 64–71.
- Jiang, L.P., Liu, P., Zhao, S.B., 2015. Magnetic ATP/FA/Poly(AA-co-AM) ternary nanocomposite microgel as selective adsorbent for removal of heavy metals from wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 470, 31–38.
- Jung, Y.C., Yoo, H.J., Kim, Y.A., *et al.*, 2010. Electroactive shape memory performance of polyurethane composite having homogeneously dispersed and covalently crosslinked carbon nanotubes. *Carbon* 48, 1598–1603.

- Kiliaris, P., Papaspyrides, C.D., 2010. Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. *Progress in Polymer Science* 35, 902–958.
- Kim, J., Wainaina, J., Na, J.S., 2011. Synthesis of amphiphilic silica/polymer composite nanoparticles as water-dispersible nano-absorbent for hydrophobic pollutants. *Journal of Industrial and Engineering Chemistry* 17, 681–690.
- Krishnan, N.N., Lee, S., Ghorpade, R.V., *et al.*, 2018. Polybenzimidazole (PBI-OO) based composite membranes using sulfophenylated TiO₂ as both filler and crosslinker, and their use in the HTPEM fuel cell. *Journal of Membrane Science* 560, 11–20.
- Laoutid, F., Bonnaud, L., Alexandre, M., *et al.*, 2009. New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Materials Science and Engineering: R: Reports* 63, 100–125.
- Lee, S.K., Kim, B.K., 2013. Synthesis and properties of shape memory graphene oxide/polyurethane chemical hybrids. *Polymer International* 63, 1197–1202.
- Lewin, M., Pearce, E.M., Levon, K., *et al.*, 2006. Nanocomposites at elevated temperatures: Migration and structural changes. *Polymers for Advanced Technologies* 17, 226–234.
- Li, J.H., Zhang, G.P., Deng, L.B., *et al.*, 2014. In situ polymerization of mechanically reinforced, thermally healable graphene oxide/polyurethane composites based on Diels–Alder chemistry. *Journal of Materials Chemistry A* 2, 20642–20649.
- Li, M., Ren, W.T., Zhang, Y., *et al.*, 2012. Study on properties of gel polymer electrolytes based on ionic liquid and amine-terminated butadiene-acrylonitrile copolymer chemically crosslinked by polyhedral oligomeric silsesquioxane. *Journal of Applied Polymer Science* 126, 273–279.
- Li, Q., Guo, L.H., Qiu, T., *et al.*, 2018. Polyurethane/polyphenylsilsequioxane nanocomposite: From waterborne dispersions to coating films. *Progress in Organic Coatings* 122, 19–29.
- Lin, C.H., Sheng, D.K., Liu, X.D., *et al.*, 2017. A self-healable nanocomposite based on dual-crosslinked graphene oxide/polyurethane. *Polymer* 127, 241–250.
- Lin, H.D., Zhao, C.J., Jiang, Y.N., *et al.*, 2011. Novel hybrid polymer electrolyte membranes with high proton conductivity prepared by a silane-crosslinking technique for direct methanol fuel cells. *Journal of Power Sources* 196, 1744–1749.
- Liu, D., Geng, L., Fu, Y.Q., *et al.*, 2010. In situ sol–gel route to novel sulfonated polyimide–SiO₂ hybrid proton-exchange membranes for direct methanol fuel cells. *Polymer International* 59, 1578–1585.
- Liu, H.D., Zhu, G.M., Zhang, C.S., 2020a. Promoted ablation resistance of polydimethylsiloxane via crosslinking with multi-ethoxy POSS. *Composites Part B* 190, 107901.
- Liu, J., Shen, Z.H., Xu, W.H., *et al.*, 2020b. Interface-strengthened polymer nanocomposites with reduced dielectric relaxation exhibit high energy density at elevated temperatures utilizing a facile dual crosslinked network. *Small* 16, 2000714.
- Liu, P., Jiang, L.P., Zhu, L.X., *et al.*, 2014a. Novel approach for attapulgite/poly(acrylic acid) (ATP/PAA) nanocomposite microgels as selective adsorbent for Pb(II) ion. *Reactive & Functional Polymers* 74, 72–80.
- Liu, P., Jiang, L.P., Zhu, L.X., *et al.*, 2014b. Novel covalently cross-linked attapulgite/poly(acrylic acid-co-acrylamide) hybrid hydrogels by inverse suspension polymerization: synthesis optimization and evaluation as adsorbents for toxic heavy metals. *Industrial & Engineering Chemistry Research* 53, 4277–4285.
- Liu, P., Jiang, L.P., Zhu, L.X., *et al.*, 2014c. Attapulgite/poly(acrylic acid) nanocomposite (ATP/PAA) hydrogels with multifunctionalized attapulgite (org-ATP) nanorods as unique cross-linker: preparation optimization and selective adsorption of Pb(II) ion. *ACS Sustainable Chemistry & Engineering* 2, 643–651.
- Liu, P., Zhu, L.X., Guo, J.S., *et al.*, 2014d. Polygorskite/polystyrene nanocomposites via facile in-situ bulk polymerization: Gelation and thermal properties. *Applied Clay Science* 100, 95–101.
- Liu, P., Jiang, L.P., Zhu, L.X., *et al.*, 2015a. Synthesis of covalently crosslinked attapulgite/poly (acrylic acid-co-acrylamide) nanocomposite hydrogels and their evaluation as adsorbent for heavy metal ions. *Journal of Industrial and Engineering Chemistry* 23, 188–193.
- Liu, Y., Kato, T., Kubo, M., *et al.*, 2015b. Annealing-promoted unidirectional migration of organic-modified nanoparticles embedded two-dimensionally in polymer thin films. *Journal of Applied Polymer Science* 132, 42760.
- Luo, X.M., Zhang, P., Liu, R., *et al.*, 2016. Preparation and physical properties of functionalized graphene/waterborne polyurethane UV-curing composites by click chemistry. *Polymer International* 65, 415–422.
- Lv, Y.T., Lu, B., Zhang, S., *et al.*, 2018. Mechanical enhancement of amine-functionalized TiO₂ reinforced polyimine composites. *Journal of Applied Polymer Science* 135, 46446.
- Massod, M.T., Alejandro-Heredia-Guerrero, J., Ceseracciu, L., *et al.*, 2017. Superhydrophobic high impact polystyrene (HIPS) nanocomposites with wear abrasion resistance. *Chemical Engineering Journal* 322, 10–21.
- Miao, L.Y., Bai, Y., Yuan, Y.F., *et al.*, 2018. Mussel-inspired strategy towards functionalized reduced graphene oxide-crosslinked polysulfone-based anion exchange membranes with enhanced properties. *International Journal of Hydrogen Energy* 43, 17461–17474.
- Nonahal, M., Rastin, H., Saeb, M.R., *et al.*, 2018. Epoxy/PAMAM dendrimer-modified graphene oxide nanocomposite coatings: Nonisothermal cure kinetics study. *Progress in Organic Coatings* 114, 233–243.
- Oh, H., Kim, Y., Kim, J., 2019. Co-curable poly(glycidyl methacrylate)-grafted graphene/epoxy composite for thermal conductivity enhancement. *Polymer* 183, 121834.
- Pan, C.O., Liu, P., 2018. Surface modification of attapulgite nanorods with nitrile butadiene rubber via thiol–ene interfacial click reaction: grafting or crosslinking. *Industrial & Engineering Chemistry Research* 57, 4949–4954.
- Patel, M., Morrell, P.R., Murphy, J.J., *et al.*, 2006. Gamma radiation induced effects on silica and on silica–polymer interfacial interactions in filled polysiloxane rubber. *Polymer Degradation and Stability* 91, 406–413.
- Periyasamy, T., Asrafali, S.P., Kim, S.-C., 2020. Investigating the effects of amine-functionalized carbon balls in a polybenzoxazine matrix. *New Journal of Chemistry* 44, 12384–12396.
- Przadka, D., Andrzejewska, E., Marcinkowska, A., 2015. Multimethacryloxy-POSS as a crosslinker for hydrogel materials. *European Polymer Journal* 72, 34–49.
- Rana, S., Cho, J.W., Tan, L.P., 2013. Graphene-crosslinked polyurethane block copolymer nanocomposites with enhanced mechanical, electrical, and shape memory properties. *RSC Advances* 3, 13796–13803.
- Ren, F., Li, Z., Xu, L., *et al.*, 2018. Large-scale preparation of segregated PLA/carbon nanotube composite with high efficient electromagnetic interference shielding and favourable mechanical properties. *Composites Part B: Engineering* 155, 405–413.
- Satti, A., Perret, A., McCarty, J.E., *et al.*, 2010. Covalent crosslinking of single-walled carbon nanotubes with poly(allylamine) to produce mechanically robust composites. *Journal of Materials Chemistry* 20, 7941–7943.
- Shabaniverki, S., Thorud, S., Suarez, J.J., 2018. Vibrationally directed assembly of micro- and nanoparticle-polymer composites. *Chemical Engineering Science* 192, 1209–1217.
- Shen, B., Zhai, W.T., Tao, M.M., *et al.*, 2013. Chemical functionalization of graphene oxide toward the tailoring of the interface in polymer composites. *Composites Science and Technology* 77, 87–94.
- Takafuji, M., Yamada, S., Ihara, H., 2011. Strategy for preparation of hybrid polymer hydrogels using silica nanoparticles as multifunctional crosslinking points. *Chemical Communications* 47, 1024–1026.
- Vesile, E., Pandele, A.M., Abdrnescu, C., *et al.*, 2019. Hema-functionalized graphene oxide: A versatile nanofiller for poly(propylene fumarate)-based hybrid materials. *Scientific Reports* 9, 18685.
- Villenas, I., Rivas, B.L., Torres, C., *et al.*, 2015. Effect of functionalized trititanate nanotubes on the properties of crosslinked cationic polymer nanocomposite. *Polymer International* 64, 1121–1127.
- Vu, M.C., Bae, Y.H., Yu, M.J., *et al.*, 2019. Thermally conductive adhesives from covalent-bonding of reduced graphene oxide to acrylic copolymer. *Journal of Adhesion* 95, 887–910.

- Wang, J.D., Jia, H.B., Ding, L.F., *et al.*, 2013. Utilization of silane functionalized carbon nanotubes-silica hybrids as novel reinforcing fillers for solution styrene butadiene rubber. *Polymer Composites* 34, 690–696.
- Wang, K., Cai, L., Wang, S.F., 2011. Methacryl-polyhedral oligomeric silsesquioxane as a crosslinker for expediting photo-crosslinking of Poly(propylene fumarate): Material properties and bone cell behaviour. *Polymer* 52, 2827–2839.
- Wang, Y.F., Song, C.P., Yu, X.H., *et al.*, 2017. Thermo-responsive hydrogels with tunable transition temperature crosslinked by multifunctional graphene oxide nanosheets. *Composites Science and Technology* 151, 139–146.
- Wang, S.H., Duan, H.F., Ma, G.Z., *et al.*, 2020. Epoxy functionalization of multiwalled carbon nanotubes for their waterborne polyurethane composite with crosslinked structure. *Journal of Coatings Technology Research* 17, 91–100.
- Wu, J.C., Wu, Z.L., Yang, H.M., *et al.*, 2014. Crosslinking of low density polyethylene with octavinyl polyhedral oligomeric silsesquioxane as the crosslinker. *RSC Advances* 4, 44030–44038.
- Xing, W., Li, H.Y., Huang, G.S., *et al.*, 2017. Graphene oxide induced crosslinking and reinforcement of elastomers. *Composites Science and Technology* 144, 223–229.
- Yang, T.J., Li, Z.L., Lyu, H.L., *et al.*, 2018. A graphene oxide polymer brush based crosslinked nanocomposite proton exchange membrane for direct methanol fuel cells. *RSC Advances* 8, 15740–15753.
- Yun, S., Im, H., Heo, Y., *et al.*, 2011. Crosslinked sulfonated poly(vinyl alcohol)/sulfonated multi-walled carbon nanotubes nanocomposite membranes for direct methanol fuel cells. *Journal of Membrane Science* 380, 208–215.
- Zhang, J.Y., Si, D., Wang, S.F., *et al.*, 2020a. Novel organic/inorganic hybrid star polymer surface-crosslinked with polyhedral oligomeric silsesquioxane. *Macromolecular Research* 28, 152–158.
- Zhang, P., Yang, X.-J., Li, P., *et al.*, 2020b. Fabrication of novel MXene (Ti_3C_2)/polyacrylamide nanocomposite hydrogels with enhanced mechanical and drug release properties. *Soft Matter* 16, 162–169.
- Zhang, W.C., Camino, G., Yang, R.J., 2017. Polymer/polyhedral oligomeric silsesquioxane (POSS) nanocomposites: an overview of fire retardance. *Progress in Polymer Science* 67, 77–125.
- Zhao, Y.L., Qi, X.W., Dong, Y., *et al.*, 2016. Mechanical, thermal and tribological properties of polyimide/nano-SiO₂ composites synthesized using an in-situ polymerization. *Tribology International* 103, 599–608.
- Zhu, L.X., Guo, J.S., Liu, P., 2016a. Effects of length and organic modification of attapulgite nanorods on attapulgite/polystyrene nanocomposite via in-situ radical bulk polymerization. *Applied Clay Science* 119, 87–95.
- Zhu, L.X., Guo, J.S., Liu, P., *et al.*, 2016b. Novel strategy for palygorskite/poly(acrylic acid) nanocomposite hydrogels from bi-functionalized palygorskite nanorods as easily separable adsorbent for cationic basic dye. *Applied Clay Science* 121–122, 29–35.
- Zhu, L.X., Liu, P., Wang, A.Q., 2014. High clay-content attapulgite/poly(acrylic acid) nanocomposite hydrogel via surface-initiated redox radical polymerization with modified attapulgite nanorods as initiator and cross-linker. *Industrial & Engineering Chemistry Research* 53, 2067–2071.
- Zhu, Z.X., Yao, H.J., Dong, J.X., *et al.*, 2019. High-mechanical-strength polyimide aerogels crosslinked with 4, 4'-oxydianiline-functionalized carbon nanotubes. *Carbon* 144, 24–31.

Thermal and Morphological Analyses of Polymer Matrix Composites

Subramani Devaraju, Vignan's Foundation for Science, Technology and Research, Guntur, India

Arumugam Hariharan, Krishnasamy Balaji, and Muthukaruppan Alagar, PSG Institute of Technology and Applied Research, Coimbatore, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

The production of polymer matrix composites is a tedious method, which includes the strategy and development, fabrication, processing, analysis, and reduction of cost. The suitable fabrication processing methods with optimal choice of polymer matrices, reinforcements (fillers) such as inorganic, organic and hybrids, fiber length, fiber weight, percentage concentration, strategy, and other parameters to be taken in to attention. Polymer matrix used as either thermosetting or thermoplastic polymers, with suitable reactive additives. Reinforcing fillers with varying nature, continuous or discontinuous geometry, and random/oriented structure are to be deliberated. Fibrous reinforcements are categorized in to one dimensional (yarn and roving), two dimensional (woven, mat, and fabric wool), and three dimensional (fabric and braid) nature (Thomas *et al.*, 2012; Shalin, 1995; Njuguna, 2016; Wang *et al.*, 2011; Devaraju and Alagar, 2018; Ratna and Karger-Kocsis, 2008; Rajak *et al.*, 2019; Barbero, 2017; Hull and Clyne, 1996; Vijay Kumar *et al.*, 2019; Wang *et al.*, 2017; Hussain and Hojjati, 2006; Soutis, 2005; Saxena and Maiti, 2020; Advani and Hsiao, 2012).

Composite materials are used in different types of engineering applications where excellent performances are warranted under harsh and hostile working environmental conditions. Such conditions, the composite materials employed are required to possess the distinctive high performance, thermal, mechanical and tribological properties with a lesser weight and a higher resistance to degradation appropriate to warrant safety and cost-effectiveness (Thomas *et al.*, 2012; Shalin, 1995; Njuguna, 2016; Wang *et al.*, 2011; Devaraju and Alagar, 2018). Polymer matrices inherently have benefits over other materials including ceramics and metals. They are extensively utilized in variety of engineering applications due to their inimitable advantages including simple production method, lightweight and ductility. Polymer matrix composites are broadly utilized over a long period. They are mostly polymer composites typically reinforced with inorganic fillers. Since, they expected to possess the combined properties of both organic matrix and inorganic filler. Further, the inorganic reinforcement also exhibits the high thermal, mechanical stability and rigidity. Similarly, the polymer matrix contributes the ductility, flexibility, and easy processing capability of the composites.

Polymer matrix composite materials consist of two or more diverse materials that are either chemically/physically networked together. Each of the constituents retains their inimitable distinctive properties. Generally, polymer matrix composites comprise of two phases viz. matrix phase (organic polymer) and reinforcement (inorganic fillers). The matrix (organic polymer) segment is the continuous phase and the inorganic reinforcement filler are either discontinuous or continuous according to their nature. The inorganic filler reinforcement is responsible for load bearing and strength properties of the composites and the polymer matrix phase holds the filler reinforcements intact with integral part of the composites with firm adhesion. The polymer matrix composites are deliberated as vibrant materials in the field of advanced composites, owing to their collective properties, such as light weight, high stiffness, good toughness, efficient strength, good thermal properties, resistance to flame, fire, weather, moisture, fouling and corrosion, and better electrical behavior (Thoppul *et al.*, 2009; Sreenivasulu *et al.*, 2018; Mostafa *et al.*, 2017; Babu *et al.*, 2018; Chung, 2017; Benzait and Trabzon, 2018; Parikh and Gohil, 2015; Mahesh *et al.*, 2020; Kumar *et al.*, 2020; Benin *et al.*, 2020; Wanasinghe *et al.*, 2020; Gan *et al.*, 2020). They are extensively used in various high performance industrial, engineering and aerospace applications (Njuguna and Pielichowski, 2003; Mangalgiri, 1999; Quilter, 2001; Ghori *et al.*, 2018; Rana and Figueiro, 2016; Hamerton and Kratz, 2018).

Polymer matrix composites (PMCs) consists of a kind of continuous or short fibers that are embedded in polymer (organic) matrix. In the case of ceramic matrix composites (CMCs), the filler is used mainly to enhance the fracture toughness, the filler in a PMCs offers better strength and stiffness. The PMCs strength properties namely mechanical strength and load bearing behaviors are contributed by the filler (fiber) reinforcement. The purpose of the polymer matrix is to effectively bond the reinforcements together and to transfer stress/load between them. The processability of PMC materials mostly be influenced by the polymer matrix. The viscosity and the service life of the polymer matrix materials are directly influenced by the impregnation of the filler materials, fabrication of composites and prepregs storage. More prominently, the fabrication methods (molding) and processing parameters of composites are predominantly insistent by the polymer matrix resin. PMCs are used in nearly most of all sectors of modern life viz., from appliance constituents to vital components of automotive parts.

PMCs are most popular owing to their cost competitive and simple and amenable production methods. Certain of the short comings, that is, inferior behavior of the PMC are lower thermal resistance and higher coefficient of thermal expansion (CTE), which are compensated by the selection and use of appropriate additives and reinforcements.

There are two types of polymer matrix materials used conventionally for the fabrication general purpose and advanced composites: Thermosetting (phenolics, epoxies, benzoxazines and etc.) and thermoplastics (polyethylene (LDPE and HDPE), polypropylene, acrylics, nylon, and etc.) due to various reasons viz., availability, amenable processing and affordable cost. Similarly, the reinforcements preferably used for the PMC are glass fiber, carbon fiber and Kevlar fiber (aramid).

Properties of Polymer Matrices and Composites

PMCs properties might be expected by the rule of combinations. PMCs are used for production of primary and secondary aerospace structural components, boat assemblies, kayaks, canoes, automotive components, radio controlled transportation, sport components (skis, golf clubs, fishing rods, tennis racquets, and etc.), bullet-proof jackets and additional armor components, clutch and brake linings.

Properties of PMCs are influenced by the chosen fibers properties, alignment of fibrous reinforcement, and weight percentage of the fibers and nature of the matrix.

Types of Reinforcements and Their Uses

Use of neat polymers (without reinforcement) as structural materials is inadequate by inferior mechanical properties, for example, the tensile strength of epoxy is about 140 MPa (20,000 psi). Moreover to somewhat low strength, polymeric materials hold lower impact resistance. Hence, the filler reinforcement of polymers by robust fibrous network permits production of PMCs considered by the subsequent properties, viz., high stiffness, better tensile strength, improved fracture toughness, very good resistance against abrasion, puncture, and corrosion and cost competitive.

Application of Polymer Matrix Composite Materials

PMCs are widely used in modern life in the form of products ranged from device components to a massive collection of automotive components owing to their inexpensive and simple and amenable fabrication techniques. Major applications of PMCs including (Jose and Joseph, 2012; Wang *et al.*, 2011):

In automotive sectors – Fabrication of panel bodies, doors, drive shaft, leaf springs, bumpers, race vehicle bodies, and etc.

In aerospace sectors – Utilized in the fabrication of primary and secondary structural components for passenger airbus, space shuttles, military aircraft, and satellite systems. The major importance of using PMCs are to reduce the weight of aircraft, which reduces the fuel consumption and improve the performance of aircraft, and to lower its costs.

In marine sector – Used to fabricate the boat/marine body components using fiber glass PMCs, kayaks, and canoes.

In sports equipments – Used in footwear, fabrication of sports components and equipment and other goods due to their lower weight and higher strength performances.

In bio-medical sectors – Used in medical implants, devices fabrication for orthopedics, body parts for MRI scanners, tables for X-rays, and prosthetics.

In electrical sectors – Electrical panels, printed circuit board, switch-gear, electrical connectors and insulators. Also used in fabrication of electronic devices including Li-ion, capacitors, and bendable batteries and portable digital equipment covers including head-phones, etc.

Protective equipment – Since PMCs can judiciously survive excessive warm or icy and other harmful conditions, they are habitually used for the preparation of bullet-proof jackets and other armor products.

Industrial – PMCs are used in the fabrication of storage container for chemicals, high pressure containers, valves and pump housing. Also PMCs are used in blades, impellers, blower and motor covers and etc.

Structural – PMCs are used to restoration of bridges (flyovers) and other erection materials and equipments, including booms, blades for wind-mill, and cranes.

Role of Polymer Composite Materials in the 21st Century

The role and some of the uses of PMC at present are listed below:

- (1) Five-axis weaving expertise for the future generation of aircraft and mechanical enactment of multi-axis weave structures.
- (2) Non-crimp fiber implements for helicopters composite components.
- (3) Non-crimp braided carbon fiber filled PMCs for aeronautic applications.
- (4) Finite element modeling of textile filled composites and relationship with-real testing.
- (5) Textile composites in ballistics: modeling the material and failure response.
- (6) 3D textile composites: mechanical-progressive failure modeling and strength predictions.
- (7) Long-term resilience of plain weaves polymer composites.

Thermal Analyses of Polymer Matrices and Composites

Thermal analyses are the significant tool to characterize the polymer composites to predict and ascertain their high temperature applications. A complete assessment of the thermal behavior of a material would requires the following analyses including DSC, TGA/DTA, and DMA.

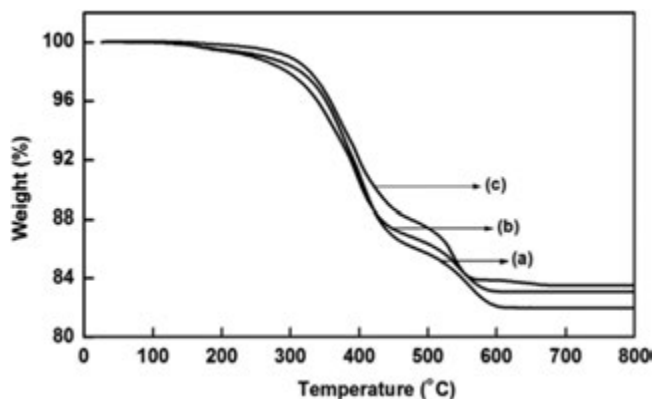


Fig. 1 TGA thermogram of epoxy hybrid composites (a) G-E, (b) Al_2O_3 + G-E, (c) Al_2O_3 + SiO_2 + ATH + G-E. Copyright 2016. Reproduced with permission from Suchitra, M., Renukappa, N.M., 2016. The thermal properties of glass fiber reinforced epoxy composites with and without fillers. *Macromolecular Symposia* 361, 117–122, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Morphological Analyses of Polymer Matrices and Composites

In order to precisely study the in-depth arrangement textural morphology and structure of the fabricated composite materials, the following analysis are performed: XRD, XPS, AFM, SEM, TEM.

Epoxy Matrix Composites

Epoxy resins are unique of the greatest predominantly used thermosetting resins for production of composite materials. Epoxy based PMCs are extensively used in variety of engineering applications including construction, aerospace, automotive, marine, oil and gas industries, owing to their cost competitive, lower weight, minimal shrinkage, good thermal and mechanical performances, superior electrical properties good strength and stiffness, long fatigue life, excellent adhesion behavior to wide range of substrates and good resistance to moisture, weather, solvent, fire and heat (Dusek, 1985; Ciesielski *et al.*, 2017; Toldy *et al.*, 2011; Vengatesan *et al.*, 2011; Devaraju *et al.*, 2013; Selvi *et al.*, 2019a; Ashok Kumar *et al.*, 2002; Alagar *et al.*, 1999; Bondzic *et al.*, 2006; Alagar *et al.*, 2000b; Nagendiran *et al.*, 2010; Alagar *et al.*, 2000a; Matykiewicz, 2020b; Sapiai *et al.*, 2020; Mittal *et al.*, 2016).

Suchitra research group reported the thermal and morphological behavior of glass fiber filled epoxy matrix composites using inorganic fillers (such as alumina, silica, and alumina trihydrate) (Suchitra and Renukappa, 2016). For the fabrication of epoxy composites they used pultrusion and ultrasonication techniques. They studied the thermal and morphological properties using DSC, TGA and SEM techniques. From DSC, the glass fiber reinforced composites possess improved values of T_g than the neat and other hybrid systems. TGA thermogram of the all the PMCs are depicted in Fig. 1. From the TGA, it is observed that GF reinforced epoxy composites exhibited good thermal stability (Initial degradation and maximum degradation) when compared to the neat epoxy system. This might be due to the presence of reinforcement in the epoxy matrix, which prevents the distribution of the volatile decomposition products.

The surface morphology and dispersion behavior of GF reinforced epoxy composites are checked with SEM and presented in Fig. 2. From SEM images, it was perceived that glass fibers are well dispersed in epoxy and arranged homogeneously. The reasonably distributed patterns were attained using the approach engaged for formulating the epoxy matrix composites.

Ghasem Naderi research group reported (Esmizadeh *et al.*, 2016) the synergistic properties of nanosized clay (NC) and carbon nanotube (CNT) filled hybrid epoxy composites and studied their thermal and morphological properties. Thermal performances of the hybrid epoxy composites were studied using TGA, HDT and DMA techniques. The thermal results obtained indicated that the developed hybrid epoxy composites showed relatively higher degradation temperature, HDT and T_g compared to those of neat system. The value of T_g increased to 123°C for 0.2% CNC introduced epoxy composites from 113°C for neat epoxy system. From TGA analysis (Fig. 3) the developed epoxy composites showed higher thermal degradation (initial degradation and maximum degradation) and char yield compared to the neat epoxy matrix. The initial degradation increased from 340°C to 344°C, T_{max} from 369°C to 375°C and residual char increased to 13% from 10% respectively. From HDT analysis, the 0.2% CNC-epoxy composites show higher values of HDT (increased by 9.7°C compared to that of pristine epoxy) than other systems. In summary, thermal performances of epoxy with 0.2% CNC and epoxy with 0.2% PNC, among them CNT the enhanced the higher values of T_g , T_d , residual char, and HDT of epoxy than those of NC. This may be due to the good compatible and dispersion nature of CNC in to epoxy when compared to those of PNC (poor dispersion). This result supports that CNT and NC have a more substantial synergistic influences in enhancing the thermal performances of the resulting CNC epoxy composites.

In order to understand the interaction between epoxy matrix and nano-fillers, SEM was performed to ascertain the surface and fractured morphology of epoxy hybrid composites and the images obtained are presented in Fig. 4. Fig. 4 shows the fractured

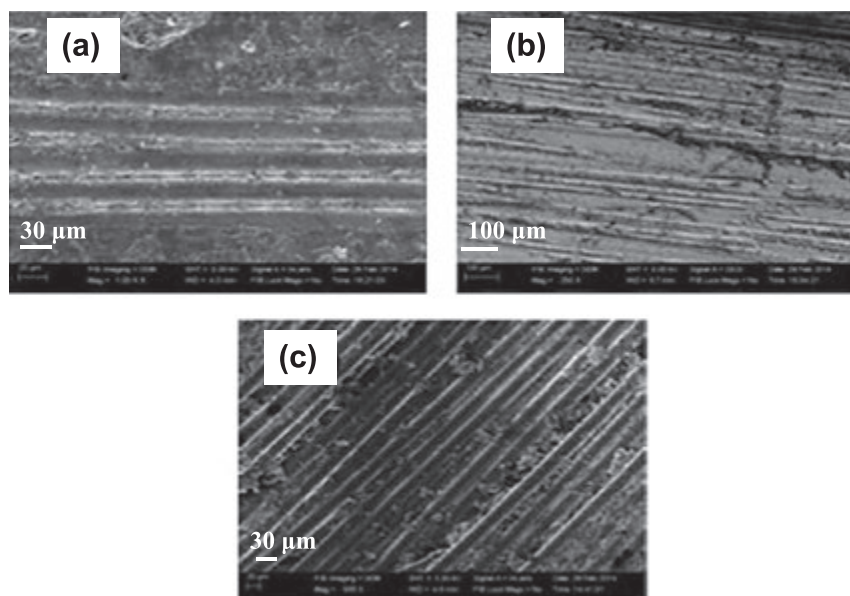


Fig. 2 SEM image of epoxy hybrid composites (a) G-E, (b) Al_2O_3 + G-E, (c) Al_2O_3 + SiO_2 + ATH + G-E. Copyright 2016. Reproduced with permission from Suchitra, M., Renukappa, N.M., 2016. The thermal properties of glass fiber reinforced epoxy composites with and without fillers. *Macromolecular Symposia* 361, 117–122, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

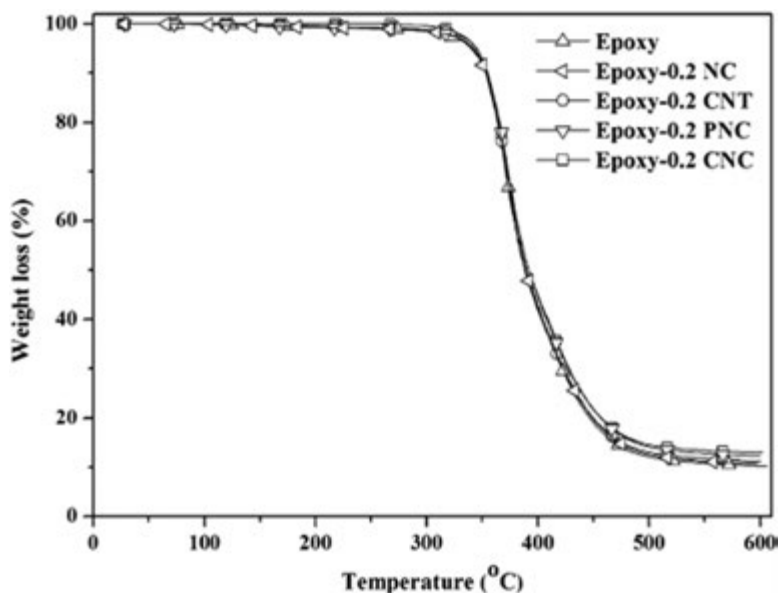


Fig. 3 TGA thermogram of epoxy composites with different nanofillers. Copyright 2015, Reproduced with permission from Esmizadeh, E., Naderi, G., Yousefi, A.A., Milone, C., 2016. Thermal and morphological study of epoxy matrix with chemical and physical hybrid of nanoclay/carbon nanotube. *JOM* 68, 362–373. Springer, The Minerals, Metals & Materials Society.

surface of the various types of filler reinforced epoxy composites. From Fig. 4(a), the fractured surface of the neat epoxy was very smooth surface while filler introduced epoxy there was a substantial increase in roughness behavior of surface. The higher surface roughness was observed for 0.2% CNC filled epoxy system when compared to that of 0.2% PNC filled epoxy system due to the efficient interaction occurred between the CNC filler and epoxy matrix. This statement is in good agreement with the values of T_g obtained from the DMA characterization.

Yasmin *et al.*, developed the various weight loaded graphite platelets reinforced epoxy composites using anhydride as curing agent and studied their structural, thermal and mechanical properties (Yasmin and Daniel, 2004). The storage modulus and T_g of the epoxy composites showed increase with increasing weight content of graphite platelet, though, the CTE values decreased. The thermal stability of the composites indicated higher thermal stability and higher char residue than that of neat epoxy matrix. From

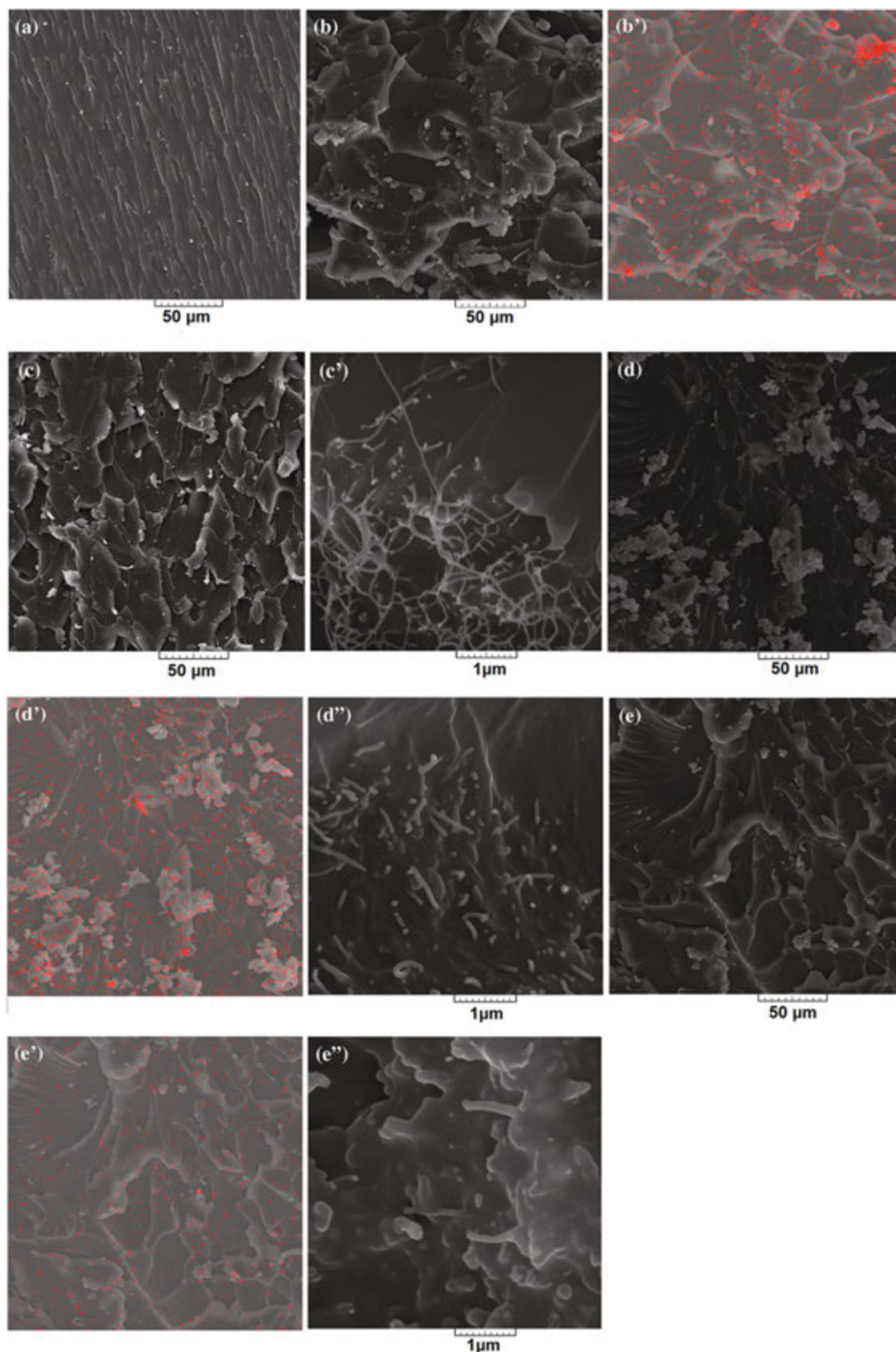


Fig. 4 Fracture surface morphology of (a) epoxy, (b) epoxy-NC, (c) epoxy-CNT, (d) epoxy-PNC and (e) epoxy-CNC by SEM. Dispersion status of NC (b') epoxy-NC, (d') epoxy-PNC and (e') epoxy-CNC with detection Si by EDX. Dispersion status of CNT: (c') epoxy-CNT, (d'') epoxy-PNC and (e'') epoxy-CNC by high-magnification SEM. Copyright 2015, Reproduced with permission from Esmizadeh, E., Naderi, G., Yousefi, A.A., Milone, C., 2016. Thermal and morphological study of epoxy matrix with chemical and physical hybrid of nanoclay/carbon nanotube. JOM 68, 362–373. Springer, The Minerals, Metals & Materials Society.

the TGA (Table 1), for neat epoxy, the T_i temperature is 360°C, while for the composites it increases to 366°C and 368°C for 2.5 wt% and 5.0 wt% platelet graphite filled epoxy systems respectively. Also, the epoxy composites show higher char residue at 800°C as the filler ratio increases. Where neat epoxy system displays a char residue of 10%, in case of composites exhibited 13% and 15% for 2.5 and 5 wt% graphite filled epoxy systems, respectively. Consequently, the introduction of platelet graphite filler in to epoxy resulted in prominent enhancement in thermal properties. This may be ascribed to the uniform dispersion of graphite filler in the composites that delays the dissemination of the volatile degradation products. The homogeneous dispersion of graphite platelet in epoxy system was checked with SEM technique. Fig. 5, displays the fractured surface of the neat epoxy matrix and 5% filler reinforced epoxy composites. For neat epoxy matrix, the crack typically pledges from surface flaws or higher stress areas. The mirror resembling area signifies the slow progress of crack-like deficiencies for neat epoxy matrix. The streaks next to the mirror resemble area are shear edges established by nucleation and transmission of micro shear regions within the epoxy matrix. While the 5% graphite filled epoxy composites displays the shear edges but only at the commencement when the crack progress rate is lower. Furthermore, the shear edges seem to be smaller and shorter compared to that of neat epoxy matrix. This might be owing to the graphite filler constrain the free rotation of polymer chains by crack tip pinning.

Mahato research group studied the thermal, mechanical, and morphological properties of Al_2O_3 nanoparticle embedded glass fiber reinforced epoxy composites (Mahato *et al.*, 2019). Thermal and morphological properties studied with DSC, DMTA and SEM analysis. From DSC and DMTA analysis, the values of T_g decreased with introduction of Al_2O_3 nanoparticles in to glass fiber reinforced epoxy (GE) composites. For 0.1 wt% Al_2O_3 -GE composites, the value of T_g decreased to 10.6°C when compared to that of neat GE matrix. Up-to 0.3 wt% Al_2O_3 -GE composites showed lower values of T_g after the increasing to 0.5% Al_2O_3 -GE composites, the value of T_g was increased. Fig. 6 show the surface morphology and dispersion ability of Al_2O_3 nanoparticles in GE. Among the composites, 0.1 wt% Al_2O_3 nanoparticles incorporated in to GE is homogeneously dispersed throughout the GE. While 0.5 wt% nano- Al_2O_3 /GE composites, the Al_2O_3 nanoparticles are showed a lot of agglomeration/aggregation in the GE composites. Generally, the higher concentration of Al_2O_3 nano-particles in to the epoxy matrix system lead to the agglomeration that diminishes nano- Al_2O_3 /epoxy interfacial interaction and ultimately results in lower strength.

Matykiewicz studied the effect of the bio-char additives (0, 2.5, 5, and 10 wt%) on the performances of carbon fiber filled bio-epoxy matrix composites (Matykiewicz, 2020a). Thermal stability composites studied with TGA in both air and inert atmosphere and the results are presented in Figs. 7 and 8 respectively. From TGA, the epoxy composites analyzed in a N_2 atmosphere, the introduction of bio-char considerably didn't affect their thermal performance. The $T_{10\%}$ degradation ascribed as on average of 330°C and the char residue at 800°C was in the range of 43%–45% (Table 1). In-case of air atmosphere; the thermal stability was increased with the increase in weight content of bio-char of epoxy matrix. The 10% weight loss was increased from 302 to 325°C, and the maximum degradation increased from 345 to 353°C.

The surface morphology of bio-char and bio-char-modified epoxy composites are studied with SEM technique and the images obtained are depicted in Fig. 9. From the SEM, bio-char was observed the size with an average diameter of 4–8 μm . In case of the bio-char filled epoxy composites observed that there is no bio-char aggregation/agglomeration, which specifies good association between bio-char and epoxy matrix (Fig. 9).

Karvanis research group developed basalt fiber reinforced epoxy matrix composites (BFRP) and studied their thermal and mechanical properties (Karvanis *et al.*, 2020). From the TGA, it is indicated that there is a sharp deterioration started at 260–300°C during the decomposition of the BFRP matrix composites both in air and inert environment and this may be due to the epoxy matrix weight loss. Compared the thermal degradation of BFRP matrix composites in air and nitrogen atmosphere, it can be observed that the basalt fibers are not affected much up to 900°C while in air atmosphere the epoxy matrix has completely vanished before the temperature of 550°C. From DTG spectra, it was observed that the maximum degradation peaks which relate to the maximum decomposition of composites. For BFRP matrix composites, in N_2 atmosphere, the peak (T_{max}) is noticed at 341°C, which is represents to the epoxy matrix degradation, while in air atmosphere, two decomposition peaks are observed at 336.4 and 458.6°C.

Kavimani research group reported the synergistic enhancement of GO and TiO_2 particles reinforced in to epoxy matrix composites through compression molding fabrication technique (Kavimani *et al.*, 2020). Thermal properties of 1.5 wt% GO reinforced composites is studied using TGA. Here, three stages of degradation were observed for GO reinforced epoxy composites. The first stage degradation arises from 30°C to 370°C with the weight loss of 23.3%. Second stage degradation started at 373°C with the weight loss of 63.3% and the final stage of degradation occurred at 470°C with the mass loss of 91.4%. Thermal degradation of composites with respect to residual char is presented in Table 1. The fractured surface morphologies of the developed epoxy matrix and epoxy composites are displayed in Fig. 10. From the SEM images, the neat epoxy (Fig. 10(a)) displays the very smooth surfaces with brittle fracture. In case of composites, the micro voids observed may be owing to de-bonding impact of filler from epoxy matrix. Rough surface fractured morphology with plenty of edges infers the existence of ductile fractured mechanism.

Dubois group reported the varying weight percentage concentration (0.1, 0.3, and 0.5 wt%) of aluminum hypophosphite ($AlPO_2$) nanofillers reinforced epoxy composites and studied their cure kinetics and thermal stability in order to utilize them for special high performance applications (Tikhani *et al.*, 2020). Cure behavior of various weight percentage concentration of AHP nanoparticles (0.1, 0.3, and 0.5 wt%) reinforced epoxy/amine system was studied using DSC with the heating rates of 5, 10, 15 and 20°C. From the Table 1, it is observed that the AHP incorporation in to epoxy matrix has subsidized to cure behavior of epoxy resin and the cure index (CI) values obtained indicates excellent cure states. Low concentration of AHP expedites the better dispersion in the epoxy matrix and inhibits physical restrictions including viscosity or dilution effect. At lower weight concentration (i.e., 0.1 wt%),

Table 1 Thermal properties of various filler reinforced epoxy matrix composites

Composites	T_g	Thermal Degradation			Weight Loss (%)	CTE ($\mu\text{m}/\text{m}^\circ\text{C}$)	Reference
		IDT	($T_{10\%}$)	T_{max}			
G-E	98	200		410	18		Suchitra and Renukappa (2016)
Al_2O_3 + G-E	126	210		415	17		Suchitra and Renukappa (2016)
Al_2O_3 + SiO_2 + ATH + G-E	103	250		425	16		Suchitra and Renukappa (2016)
Epoxy	113	340		369	10		Esmizadeh <i>et al.</i> (2016)
0.2% NC + Epoxy	121	343		372	11		Esmizadeh <i>et al.</i> (2016)
0.2% CNT + Epoxy	121	341		370	11		Esmizadeh <i>et al.</i> (2016)
0.2% PNC + Epoxy	121	343		374	12		Esmizadeh <i>et al.</i> (2016)
0.2% CNC + Epoxy	123	344		375	13		Esmizadeh <i>et al.</i> (2016)
Neat DGEBA Epoxy		305 $\pm$ 1		407 $\pm$ 1.5	10 $\pm$ 2		Yasmin and Daniel (2004)
2.5 wt% Graphite/Epoxy		318 $\pm$ 5		412 $\pm$ 2	13 $\pm$ 4		Yasmin and Daniel (2004)
5.0 wt% Graphite/Epoxy		330 $\pm$ 2		414 $\pm$ 3	15 $\pm$ 4		Yasmin and Daniel (2004)
BC	–		528.9	–	82.9		Matykiewicz (2020a)
0 BC	73 $\pm$ 2		329.5	355.6	45.57		Matykiewicz (2020a)
2.5 BC	73 $\pm$ 2		331.1	359.1	42.00		Matykiewicz (2020a)
5 BC	71 $\pm$ 2		329	360.2	42.89		Matykiewicz (2020a)
10 BC	73 $\pm$ 2		329.5	358.8	44.18		Matykiewicz (2020a)
BC			396.4	507.9	4.92		Matykiewicz (2020a)
0 BC			302.6	345.1	1.0		Matykiewicz (2020a)
2.5 BC			317.2	346.5	0.9		Matykiewicz (2020a)
5 BC			318.3	350.2	0.5		Matykiewicz (2020a)
10 BC			324.9	353.4	0.1		Matykiewicz (2020a)
1.5 wt% Go/ TiO_2 -Epoxy		142	379		8.8		Kavimani <i>et al.</i> (2020)
Epoxy	73.2	319	351		9.8		Tikhani <i>et al.</i> (2020)
E-0.1% AHP	79.5	320	348		9.0		Tikhani <i>et al.</i> (2020)
E-0.3% AHP	73.1	295	343		9.4		Tikhani <i>et al.</i> (2020)
E-0.5% AHP	69.5	299	337		10.7		Tikhani <i>et al.</i> (2020)
Epoxy	64.2	359		380	6.2	226.2	Allothman <i>et al.</i> (2020)
A	60.4	323		370	15.9	171.5	Allothman <i>et al.</i> (2020)
AA	65.0	311		368	13.8	226.3	Allothman <i>et al.</i> (2020)
G	62.2	316		372	13.3	207.1	Allothman <i>et al.</i> (2020)
L	61.6	329		370	22.5	104.6	Allothman <i>et al.</i> (2020)
Epoxy/CNT-0	118				28.3		Kuan <i>et al.</i> (2010)
Epoxy/CNT-1	109				29.0		Kuan <i>et al.</i> (2010)
Epoxy/CNT-3	134				32.6		Kuan <i>et al.</i> (2010)
Epoxy/CNT-5	156				39.7		Kuan <i>et al.</i> (2010)
Epoxy/CNT-7	160				40.5		Kuan <i>et al.</i> (2010)
Epoxy/CNT-9	Undetected				46.9		Kuan <i>et al.</i> (2010)
Neat Epoxy	162	372 ^a			0		Kanimozhi <i>et al.</i> (2013)
0.5% GM-epoxy	168	329 ^a			3.9		Kanimozhi <i>et al.</i> (2013)
1.0% GM-epoxy	173	337 ^a			8.3		Kanimozhi <i>et al.</i> (2013)
1.5% GM-epoxy	176	353 ^a			12.1		Kanimozhi <i>et al.</i> (2013)
DDM/EP	166	318.1 ^a			0		Sethuraman <i>et al.</i> (2014)
1% POSS-DDM/EP	175	330.4 ^a			3.5		Sethuraman <i>et al.</i> (2014)
3% POSS-DDM/EP	181	354.9 ^a			16.8		Sethuraman <i>et al.</i> (2014)
5% POSS-DDM/EP	177	371.2 ^a			10.7		Sethuraman <i>et al.</i> (2014)
BPA/EP	178	307.5 ^a			0		Sethuraman <i>et al.</i> (2014)
1% POSS-BPA /EP	185	310.9 ^a			0		Sethuraman <i>et al.</i> (2014)
3% POSS-BPA /EP	187	313.5 ^a			0		Sethuraman <i>et al.</i> (2014)
5% POSS-BPA /EP	184	319.5 ^a			0		Sethuraman <i>et al.</i> (2014)
CPA/EP	158	192.0 ^a			0		Sethuraman <i>et al.</i> (2014)
1% POSS-CPA /EP	174	200.1 ^a			0		Sethuraman <i>et al.</i> (2014)
3% POSS-CPA /EP	185	274.1 ^a			23.6		Sethuraman <i>et al.</i> (2014)
5% POSS-CPA /EP	169	319.5 ^a			24.8		Sethuraman <i>et al.</i> (2014)
OMA/EP	156	319.5 ^a			0		Sethuraman <i>et al.</i> (2014)
1% POSS-OMA /EP	168	331.8 ^a			0		Sethuraman <i>et al.</i> (2014)
3% POSS-OMA /EP	172	339.9 ^a			7.2		Sethuraman <i>et al.</i> (2014)
5% POSS-OMA /EP	166	346.0 ^a			14.0		Sethuraman <i>et al.</i> (2014)
CE/EP	234	420			19.7		Chandramohan <i>et al.</i> (2012)

Table 1 Continued

Composites	T_g	Thermal Degradation			Weight Loss (%)	CTE ($\mu\text{m}/\text{m}^\circ\text{C}$)	Reference
		IDT	$(T_{10}\%)$	T_{max}			
1% OAPS-CE/EP	246	411			21.5		Chandramohan <i>et al.</i> (2012)
3% OAPS-CE/EP	251	405			23.1		Chandramohan <i>et al.</i> (2012)
5% OAPS-CE/EP	255	398			26.3		Chandramohan <i>et al.</i> (2012)
10% OAPS-CE/EP	238	390			30.5		Chandramohan <i>et al.</i> (2012)
1% OG-POSS-CE/EP	238	408			24.2		Chandramohan <i>et al.</i> (2012)
3% OG-POSS-CE/EP	245	396			26.9		Chandramohan <i>et al.</i> (2012)
5% OG-POSS-CE/EP	233	386			29.5		Chandramohan <i>et al.</i> (2012)
10% OG-POSS-CE/EP	227	379			33.6		Chandramohan <i>et al.</i> (2012)

^a $T_{20\%}$ weigh loss.

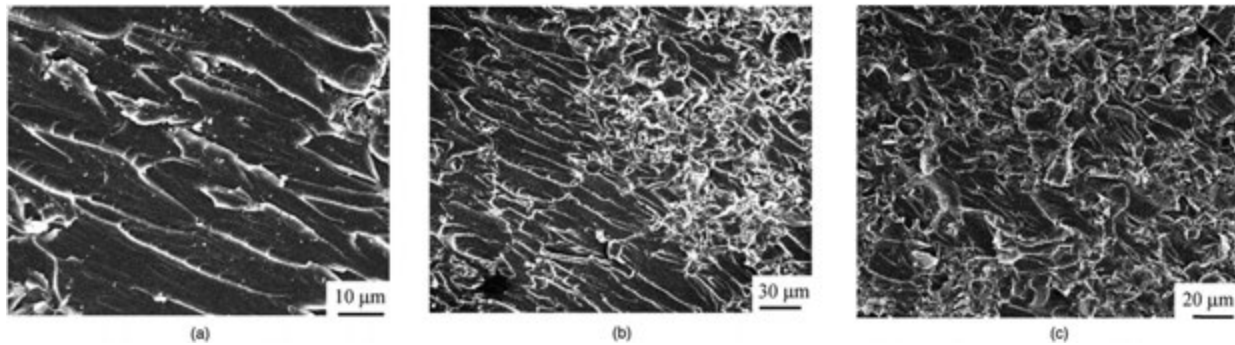


Fig. 5 SEM micrographs of 5 wt% graphite/epoxy composites. (a) Slow crack growth region, (b) transition from slow to fast fracture region and (c) fast fracture region. Copyright 2014, Reproduced with permission from Yasmin, A., Daniel, I.M., 2004. Mechanical and thermal properties of graphite platelet/epoxy composites. Polymer 45, 8211–8219, from Elsevier.

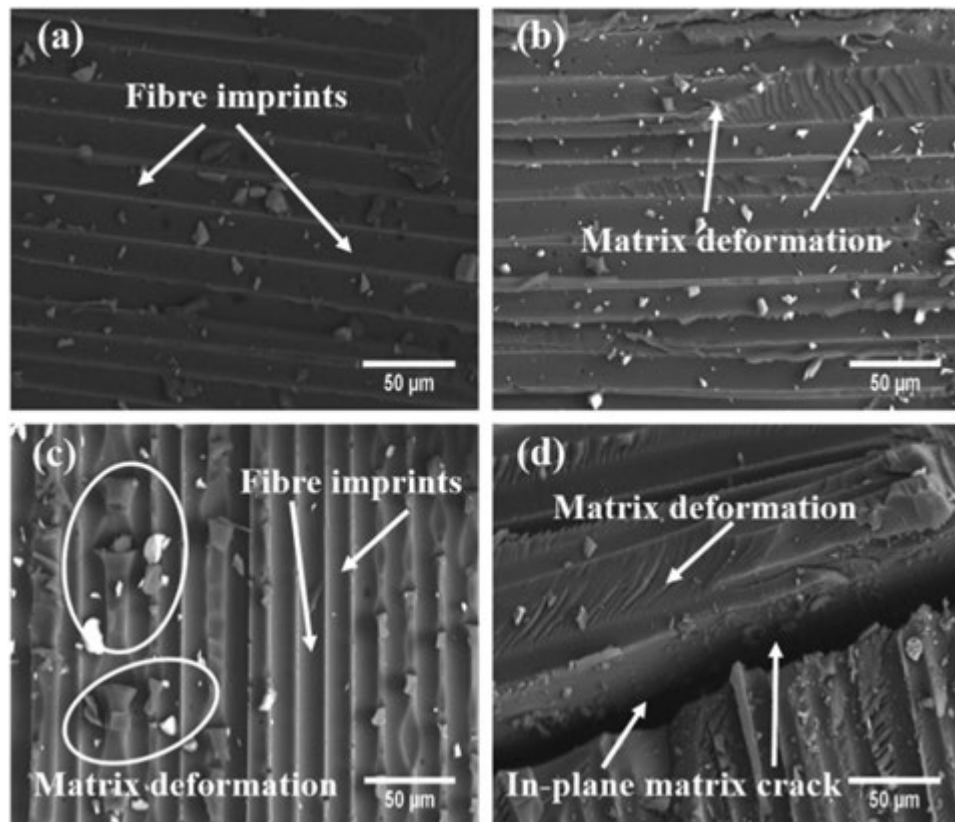


Fig. 6 SEM images of the GE composites with (a) 0 wt%, (b) 0.1 wt%, (c) 0.3 wt% and (d) 0.5% nano- Al_2O_3 content at room temperature. Copyright 2019, Reproduced with permission from Mahato, K.K., Dutta, K., Ray, B.C., 2019. Assessment of mechanical, thermal and morphological behavior of nano- Al_2O_3 embedded glass fiber/epoxy composites at in-situ elevated temperatures. Composites Part B: Engineering 166, 688–700, from Elsevier.

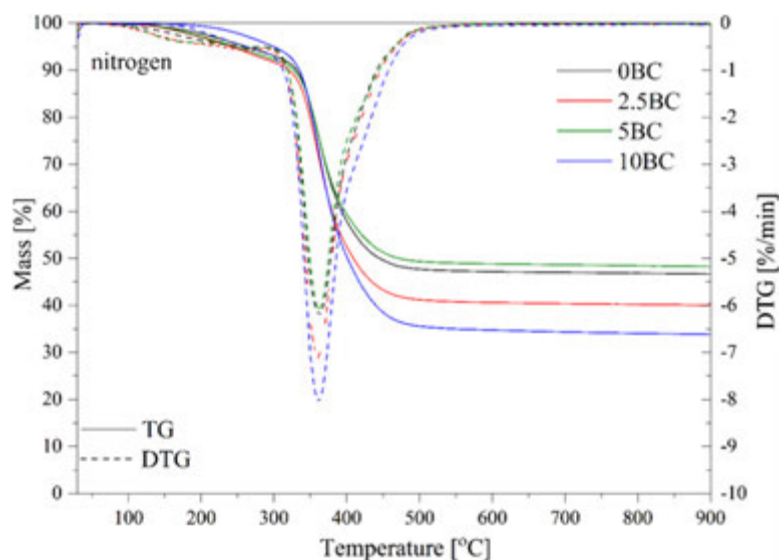


Fig. 7 TGA and DTG thermogram of bio-char carbon fiber-reinforced bio-epoxy composites in a nitrogen atmosphere. Copyright 2020, Reproduced with permission from Matykiewicz, D., 2020a. Biochar as an effective filler of carbon fiber reinforced bio-epoxy composites. Processes 8 (724), 1–13, from MDPI.

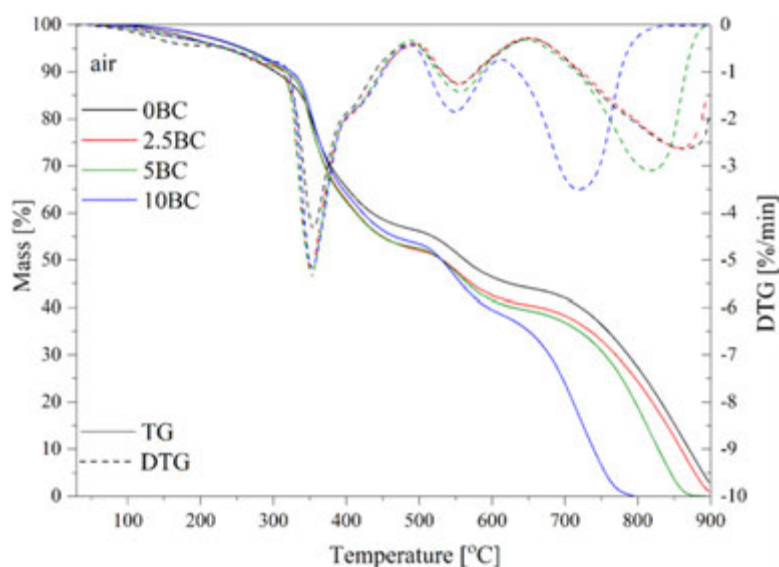


Fig. 8 TGA and DTG thermogram of bio-char carbon fiber-reinforced bio-epoxy composites in an air atmosphere. Copyright 2020, Reproduced with permission from Matykiewicz, D., 2020a. Biochar as an effective filler of carbon fiber reinforced bio-epoxy composites. Processes 8 (724), 1–13, from MDPI.

the abated amount of aggregation, and at higher weight percentages (0.3 and 0.5 wt%), several dynamic sites presented in to the system are the reasons for excellent cure states. The value of T_g of cured AHP/epoxy composites was checked between 15°C and 250°C and the results obtained were compared with neat epoxy matrix (Table 1). The value of T_g is increased to 79.5°C from 73.2°C (neat epoxy matrix) for 0.1 wt% AHP/epoxy system, in the case of 0.5 wt% AHP/epoxy system the value of T_g was decreased to 69.5°C and this may explained due to the accumulation of AHP in the epoxy which could facilitates the molecular movement. For 0.3 wt% AHP/epoxy system also exhibits the similar T_g value (73.1°C) to that of epoxy system. The thermal properties of epoxy matrix and AHP/epoxy composites was checked using TGA and the values are presented in Table 1. The initial degradation temperature is lower for AHP/epoxy composites than that of the neat epoxy matrix and this may be due to the O=P–O bond (higher activity) when compared to that of C–O and C–C bonds in present in epoxy matrix, which is enhanced by higher concentration of AHP filler content and this contributes to lower initial degradation temperature. In case of char residue the 0.5 wt% AHP/epoxy composites shows the higher char residue (10.7%) when compared to that of other systems.

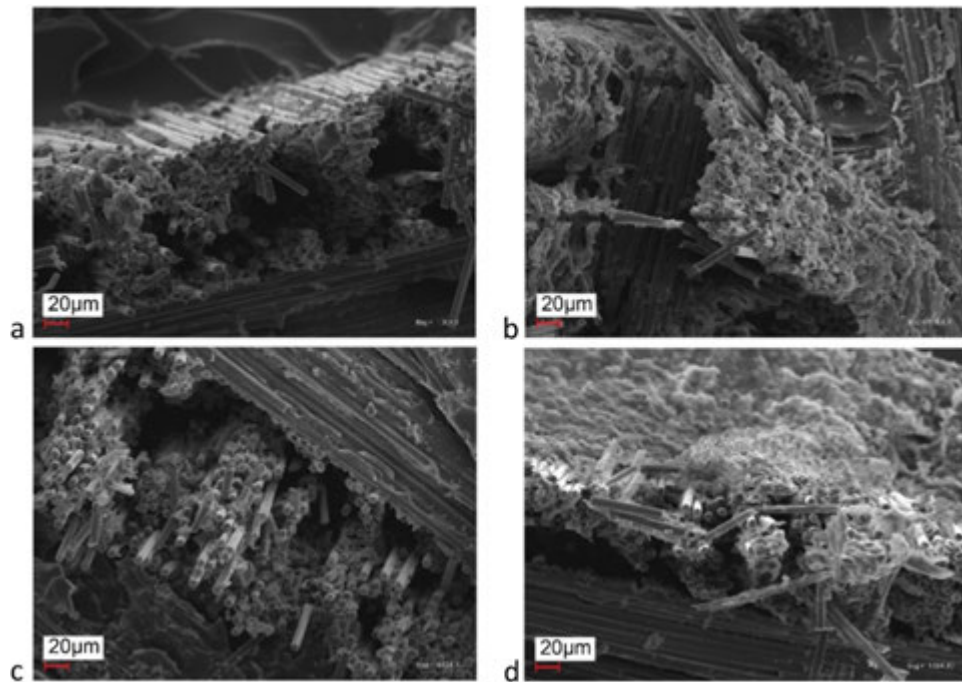


Fig. 9 SEM images of bio-char carbon fiber-reinforced bio-epoxy composite (a) 0 BCE, (b) 2.5 BCE, (c) 5 BCE, (d) 10 BCE. Copyright 2020, Reproduced with permission from Matykiewicz, D., 2020a. Biochar as an effective filler of carbon fiber reinforced bio-epoxy composites. Processes 8 (724), 1–13, from MDPI.

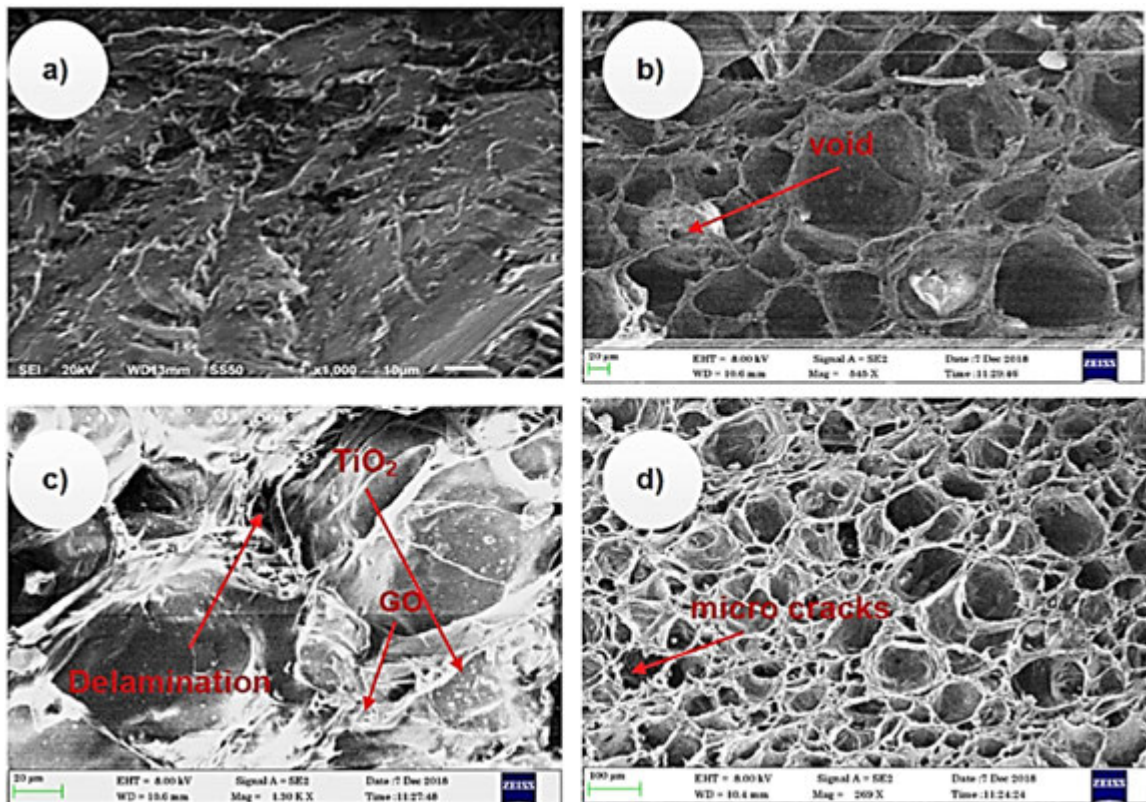


Fig. 10 SEM fracture surface morphology of (a) Neat Epoxy (b) 0.5 wt% nano filler. (c) 1 wt% nano filler (d) 1.5 wt% nano filler. Copyright 2020, Reproduced with permission from Kavimani, V., Prakash, K.S., Thankachan, T., Udayakumar, R., 2020. Synergistic improvement of epoxy derived polymer composites reinforced with graphene oxide (GO) plus titanium di oxide (TiO_2). Composites Part B: Engineering 191, 107911, from Elsevier.

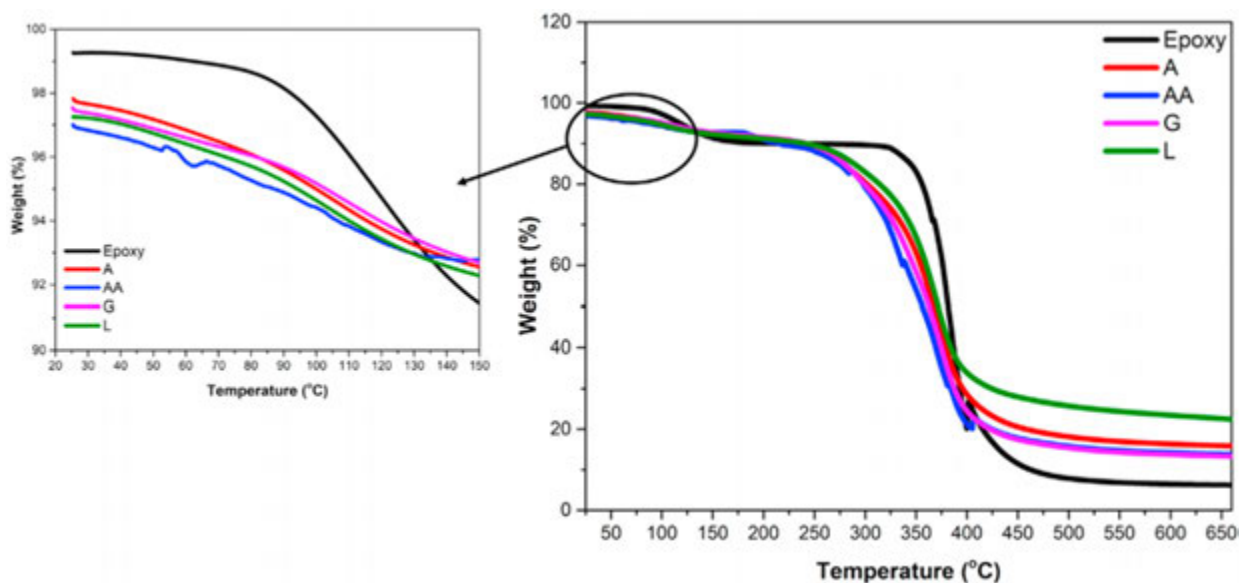


Fig. 11 TGA thermogram of neat epoxy matrix and date palm fiber (DPF) reinforced epoxy composites. Copyright 2020, Reproduced with permission from Alothman, O.Y., Jawaid, M., Senthilkumar, K., *et al.*, 2020 Thermal characterization of sate palm/epoxy composites with fillers from different parts of the tree. *Journal of Materials Research and Technology* 9, 15537–15546, from Elsevier.

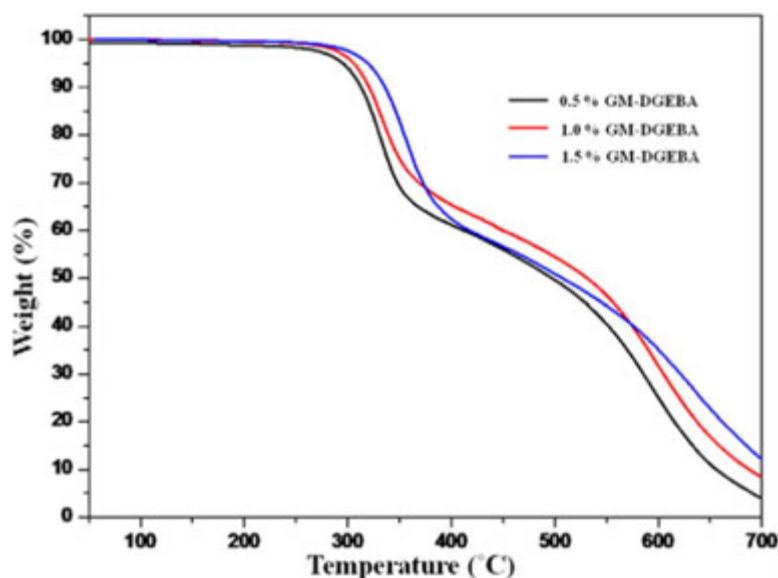


Fig. 12 TGA thermogram of functionalized mullite fiber reinforced epoxy nanocomposites. Copyright 2013, Reproduced with permission from Kanimozhi, K., Devaraju, S., Vengatesan, M.R., Selvaraj, V., Alagar, M., 2013. Studies on synthesis and characterization of surface-modified mullite fibre-reinforced epoxy nanocomposites. *High Performance Polymers* 25, 658–667, from SAGE Publications.

Jawaid research group developed the date palm fiber (DPF) reinforced epoxy composites (Alothman *et al.*, 2020) with fillers derived from palm tree portions including leaf sheath, leaf stalk, tree trunk, and fruit bunch stalk. Fig. 11 displays the TGA thermograms of the neat epoxy matrix and DPF composites. It was noticed that the DPF fibers reinforced with epoxy with different portions of the palm tree exhibit together the initial thermal degradation and maximum thermal degradation temperature were significantly lower than that of the neat epoxy matrix system. This might be owing to the decomposition of DPF fiber components including lignin, hemicellulose, and cellulose. Nevertheless, 2–3 times higher char residue values for the DPF/epoxy composites than that of the neat epoxy matrix. Among all, fibers acquired with tree trunk (L) was observed as better thermal stability (char residue of 22%) than compared to that of other systems. The values of T_g are observed between 60 and 65 °C for the neat epoxy matrix and composites and the results are presented in Table 1. Here, T_g values were found to be slightly lower due to the

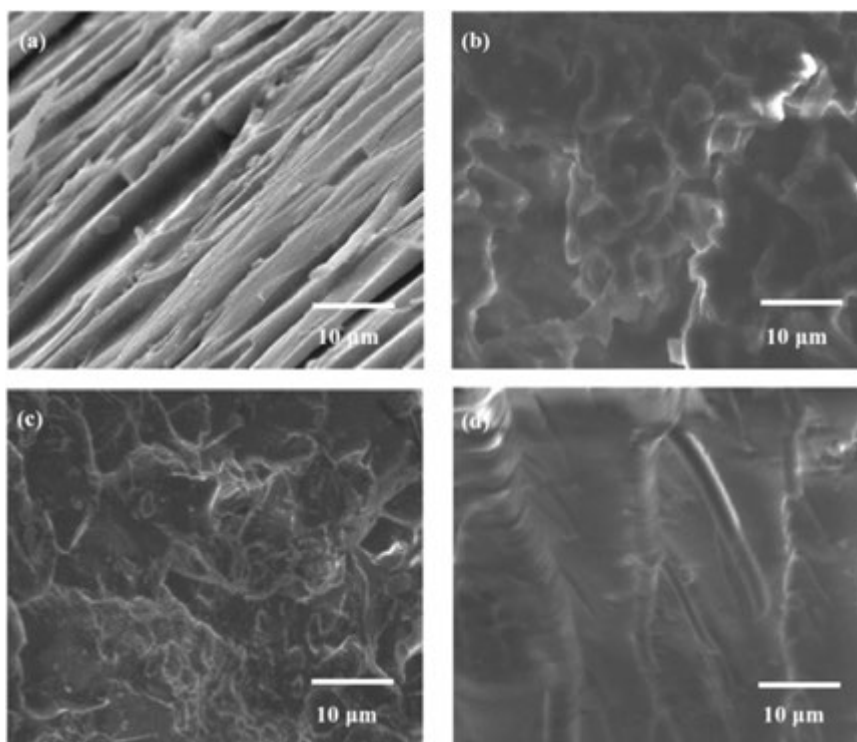


Fig. 13 SEM images of (a) neat DGEBA, (b) 0.5% GM fiber-DGEBA, (c) 1% GM fiber-DGEBA and (d) 1.5% GM fiber-DGEBA. Copyright 2013, Reproduced with permission from Kanimozhi, K., Devaraju, S., Vengatesan, M.R., Selvaraj, V., Alagar, M., 2013. Studies on synthesis and characterization of surface-modified mullite fibre-reinforced epoxy nanocomposites. High Performance Polymers 25, 658–667, from SAGE Publications.

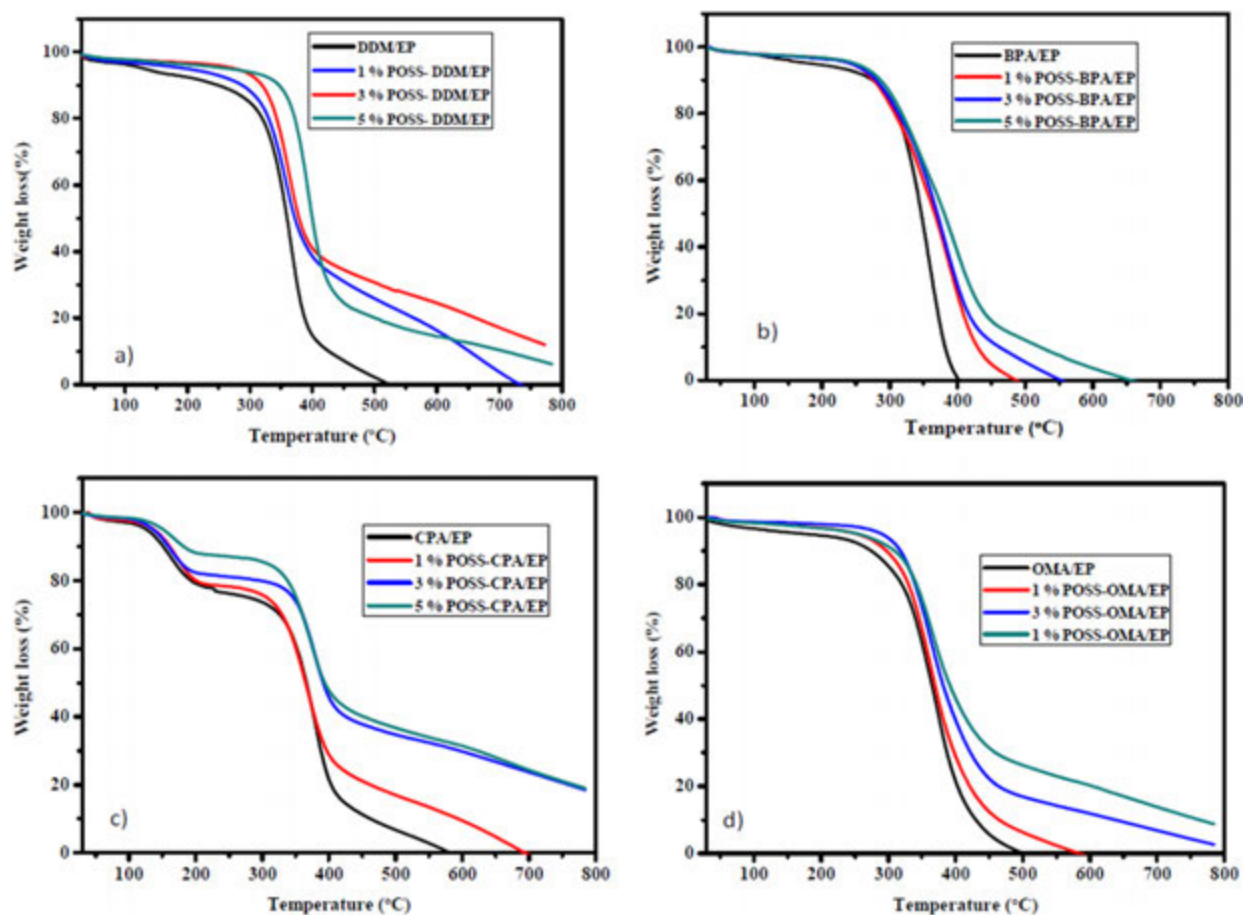


Fig. 14 TGA thermogram of POSS reinforced epoxy composites. Copyright 2014, Reproduced with permission from Sethuraman, K., Prabunathan, P., Alagar, M., 2014. Thermo-mechanical and surface properties of POSS reinforced structurally different diamines cured epoxy nanocomposites. RSC Advances 4, 45433–45441, from RSC Publications.

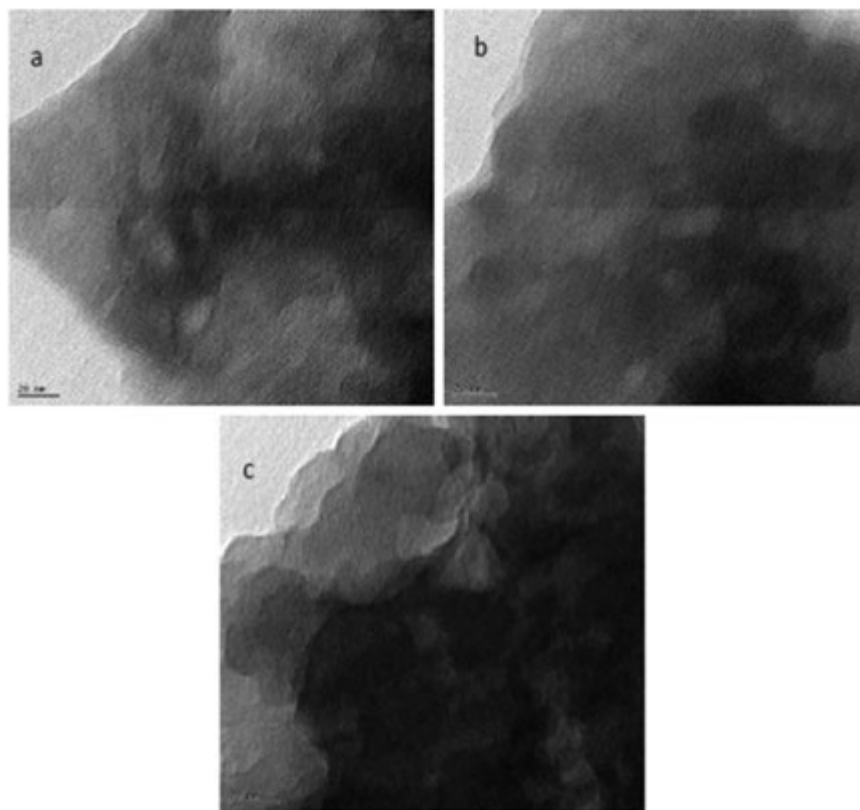


Fig. 15 TEM micrograph of 1%, 3% and 5% POSS reinforced CPA diamines cured epoxy matrix. Copyright 2014, Reproduced with permission from Sethuraman, K., Prabunathan, P., Alagar, M., 2014. Thermo-mechanical and surface properties of POSS reinforced structurally different diamines cured epoxy nanocomposites. RSC Advances 4, 45433–45441, from RSC Publications.

reinforcement of DPF fiber into the epoxy matrix. Further, CLTE of the composites beyond the T_g is reliant on the enlargement of free volume, which relates to the dimension changes in the materials under load. Enlargement of the free volume over the T_g consequences in the lower in density, enhanced chain flexibility and more number of conformational changes in the polymer chains. Consequently, the thermal enlargement is larger in the epoxy system resulted in CLTE values are increased. In contrast, filler reinforced composites systems possessed the lower values of CLTE ([Table 1](#)).

Chiang *et al.* reported the development of functionalized carbon nanotubes (CNTs) reinforced epoxy composites and studied their thermal and flame resistant properties ([Kuan *et al.*, 2010](#)). CNT is functionalized with triethoxyvinylsilane (VTES). TGA and DSC characterization techniques are utilized to check the thermal performance of epoxy composites. The value of T_g increased to 160°C from 118°C and residual char of 9 wt% CNT epoxy composites was improved by 46.94% at 750°C. The integral procedural decomposition temperature (IPDT) was increased to 1571°C from 890°C. The LOI of epoxy composites was enhanced to 27 from 22 and the UL-94 altered to V-0 from V-1 when the CNT concentration increased over the 3 wt%. The developed epoxy composites can encounter to the desires of phosphorus-free and halogen-free environmental friendly flame-retardant materials for various applications.

Alagar research group reported the varying weight content (0.5, 1.0 and 1.5 wt%) of glycidyl functionalized mullite (GM) fiber reinforced epoxy composites and studied their thermal and mechanical properties ([Kanimozhi *et al.*, 2013](#)). The mullite fiber was prepared through sol–gel techniques and its surface was functionalized with 3-glycidoxypropyltrimethoxysilane. The data acquired from the various techniques revealed that the GM fiber filled epoxy nano-composites superior properties than the neat epoxy matrix. The 20 wt% weight degradation temperature of neat epoxy matrix, 0.5, 1.0 and 1.5 wt% GM reinforced DGEBA epoxy composites arises at the weight loss temperatures of 372, 329, 337 and 353°C, respectively ([Fig. 12](#)). The values of char yield obtained for the neat epoxy and GM fiber filled epoxycomposites are 0, 3.9, 8.9 and 12.1 at 700°C respectively.

The surface morphology of the neat epoxy matrix and the mullite fiber filled epoxy composites was studied by SEM and are presented in [Fig. 13](#). From SEM analysis, the neat epoxy system shows the smooth and fractured glassy surface indicated the brittle behavior. The SEM images of fiber reinforced epoxy composites clearly evidences mullite fibers are homogeneously dispersed throughout epoxy matrix with no cavity and no phase separation.

The same research group reported the NH_2 -POSS reinforced epoxy composites using structurally modified diamines used as curative ([Sethuraman *et al.*, 2014](#)). Data acquired from thermal, mechanical, electrical and surface properties were compared with the neat epoxy matrix. [Fig. 14](#) and [Table 1](#) shows the thermal decomposition properties of DDM, OMA, CPA and BPA cured epoxy

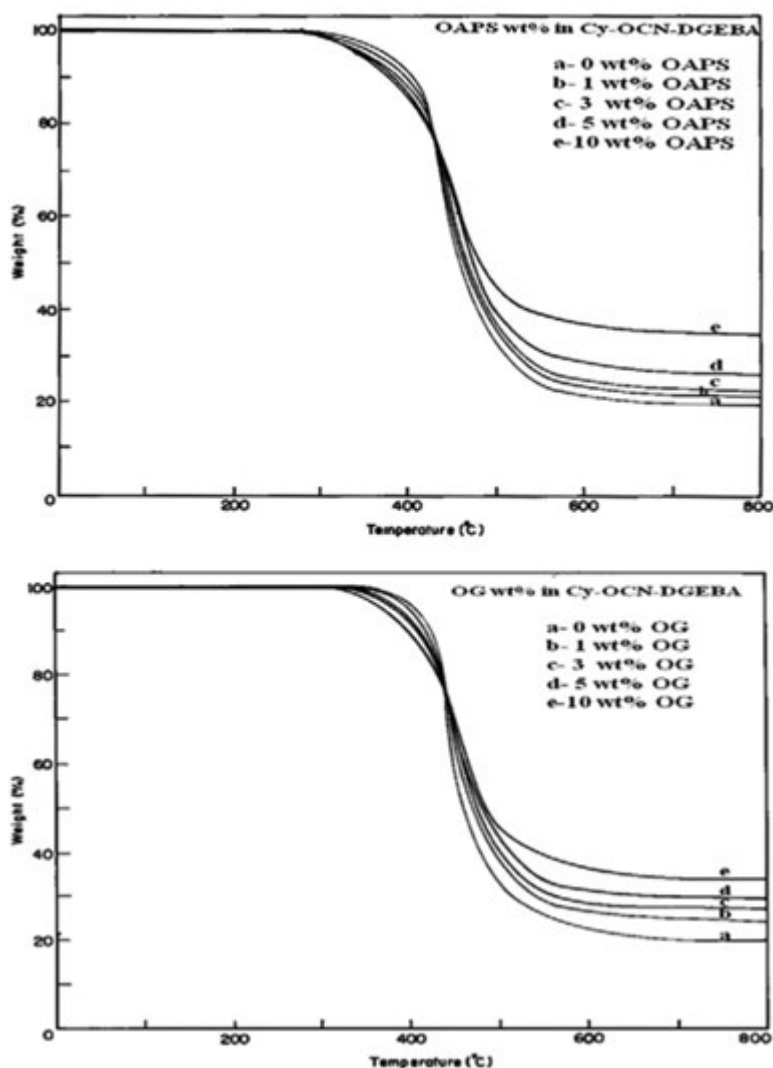


Fig. 16 TGA thermogram of neat CE/EP and OAPS/OG-POSS reinforced CE/EP nanocomposites. Copyright 2012, Reproduced with permission from Chandramohan, A., Dinkaran, K., Ashok Kumar, A., Alagar, M., 2012. Synthesis and characterization of epoxy modified cyanate ester POSS nanocomposites. High Performance Polymers 24, 405–417, from SAGE Publications.

matrices and POSS filled epoxy composites. From the results, it can be observed that epoxy matrices cured with all prepared diamine curatives have zero (0%) percent residual char at 700°C. While POSS filled epoxy systems increased the residual char agreeing to the percentage weight content of POSS loading, the 5 wt% POSS filled CPA amine cured epoxy system showed highest thermal stability with the char residue value of 25% at 700°C. TEM micrograph (Fig. 15) explains the homogeneous dispersion of POSS cages in the epoxy matrix with uniformity and it subsidizes to the better thermal and mechanical performances of the resulting composites.

Alagar research group reported the octa-functional polyhedral oligomeric silsesquioxanes [octaamino (OAPS) and octaglycidyl (OG)] reinforced epoxy modified cyanate ester nanocomposites prepared and studied the thermal and mechanical properties. From the values of T_g (Table 1) of neat CE/EP system is 234°C, while the introduction of OAPS and OG-POSS into CE/EP systems, the values of T_g increased up to 5 wt% (T_g – 251°C) and further addition of OAPS and OG-POSS decreased the T_g values of the composites. The TGA of neat CE/EP and POSS filled CE/EP composites are presented in Table 1 and Fig. 16 from the temperature range of 30–800°C. For the POSS composites system showed the $T_5\%$ weight loss decomposition temperature decreased (from 420°C to 379°C), while the residual char yield (increased to 33.6% from 19.7%) increased with an increasing the weight percentages of POSS. This might be owing to the inert silica layer in the POSS which act as protecting layer to prevent the further degradation of polymer matrix.

Surface morphology of CE/EP and POSS filled CE/EP systems are studied with XRD, SEM and TEM analysis. From XRD, the POSS reinforced system showed uniform dispersion with amorphous in nature. The fractured surfaces morphology of the neat CE/EP matrix and POSS composites systems obtained from SEM analysis are presented in Fig. 17. The morphology of the neat

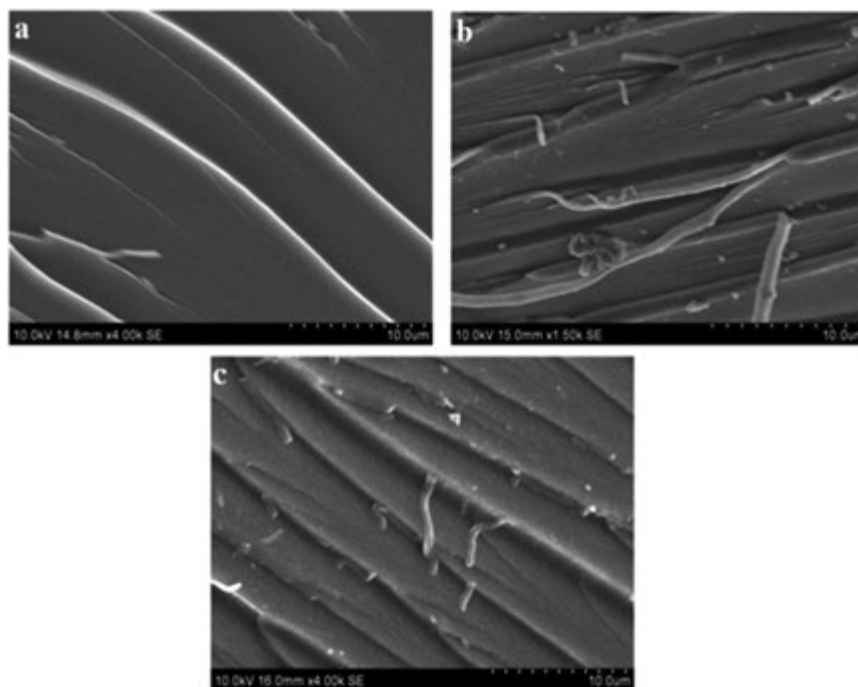


Fig. 17 SEM morphology of (a) neat CE/EP matrix (b) 5 wt% of OAPS filled CE/EP and (c) 5 wt% of OG-POSS filled CE/EP composites. Copyright 2012, Reproduced with permission from Chandramohan, A., Dinkaran, K., Ashok Kumar, A., Alagar, M., 2012. Synthesis and characterization of epoxy modified cyanate ester POSS nanocomposites. High Performance Polymers 24, 405–417, from SAGE Publications.

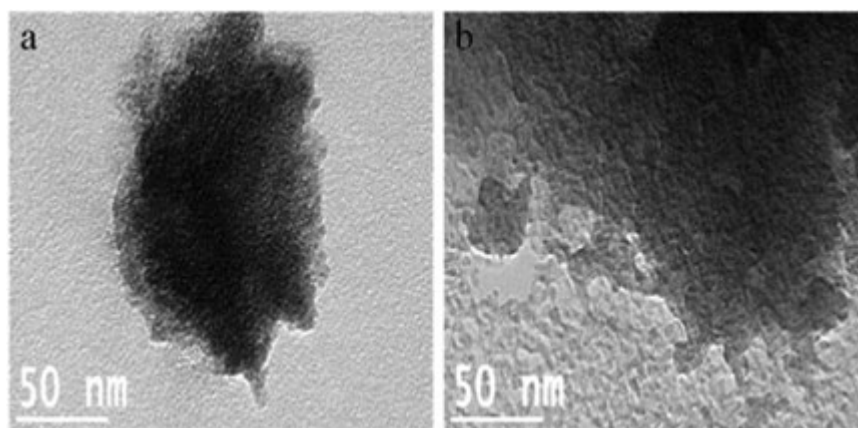


Fig. 18 TEM image of (a) 5 wt% of OAPS and (b) 5 wt% of OG-POSS filled CE/EP composites. Copyright 2012, Reproduced with permission from Chandramohan, A., Dinkaran, K., Ashok Kumar, A., Alagar, M., 2012. Synthesis and characterization of epoxy modified cyanate ester POSS nanocomposites. High Performance Polymers 24, 405–417, from SAGE Publications.

CE/EP matrix shows smooth morphology and without any micro phase separation. For POSS filled composites shows the presence of a lot of “filari” shape looks like bamboo when they were pulled out. In addition the POSS cages were homogeneously dispersed in the CE/EP matrix. Further this was checked with TEM and the TEM images of the POSS filled CE/EP composites are depicted in Fig. 18. It is also observed from TEM analysis that POSS cages are dispersed homogeneously throughout the CE/EP matrix.

Benzoxazine Matrix Composites

Polybenzoxazines (PBZs) have received much great interest and consideration owing to their numerous beneficial properties connected with traditional phenolics, including outstanding chemical and heat resistance, flame and fire retardant, low K

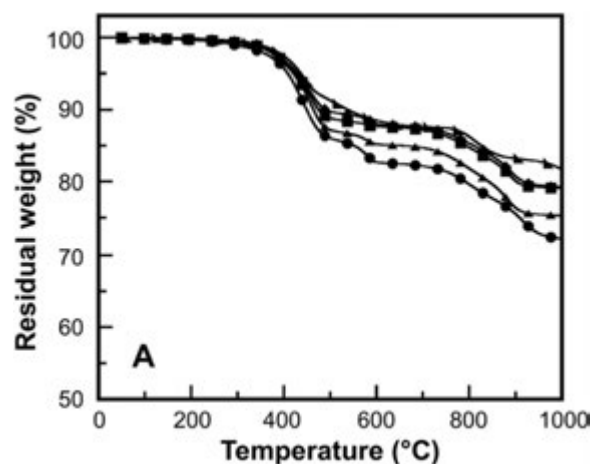


Fig. 19 TGA thermograms of aramid pulp/carbon fiber filled PBZ composites at various aramid pulp: carbon fiber mass ratios (A) of 100:0 (●), 75:25 (▲), 50:50 (■), 25:75 (◆), and 0:100. Copyright 2019, Reproduced with permission from Lertwassana, W., Parnklang, T., Mora, P., Jubsilp, C., Rimdusit, S., 2019. High performance aramid pulp/carbon fiber-reinforced polybenzoxazine composites as friction materials. Composites Part B: Engineering 177 (1–10), 107280, from Elsevier.

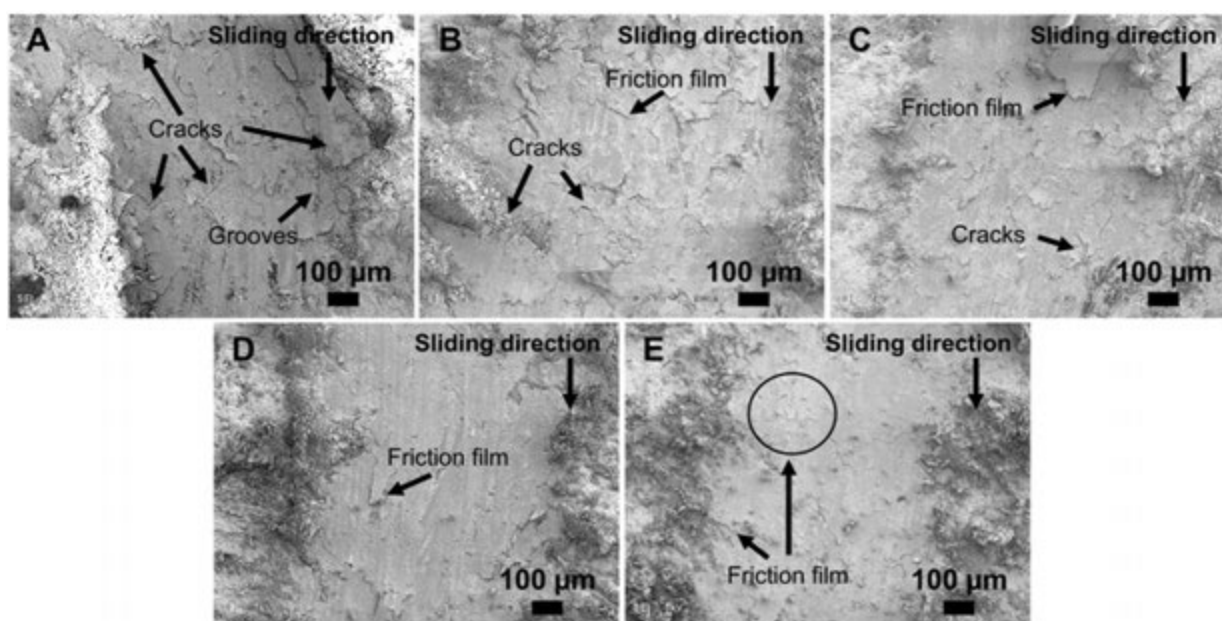


Fig. 20 SEM micrographs of aramid pulp: carbon fiber filled (A) 100:0, (B) 75:25, (C) 50:50, (D) 25:75, (E) 0:100 PBZ composites. Copyright 2019, Reproduced with permission from Lertwassana, W., Parnklang, T., Mora, P., Jubsilp, C., Rimdusit, S., 2019. High performance aramid pulp/carbon fiber-reinforced polybenzoxazine composites as friction materials. Composites Part B: Engineering 177 (1–10), 107280, from Elsevier.

dielectric, better mechanical stability, and reasonably low cost. Also they retain additional anticipated properties including minimal or no shrinkage during curing, low absorption of moisture, better dimensional stability, brilliant fire, smoke, toxicity (FST) properties, and vast molecular flexibility in the design (Kiskan, 2018; Ghosh *et al.*, 2007; Ishida and Froimowicz, 2017; Ishida and Agag, 2017; Santhosh Kumar and Reghunadhan Nair, 2010; Devaraju *et al.*, 2019b; Lyu and Ishida, 2019; Iuliana *et al.*, 2019; Sarawut *et al.*, 2013; Ramdani, 2017; Selvi *et al.*, 2019b; Devaraju *et al.*, 2019a; Krishnadevi *et al.*, 2019; Jamrozik *et al.*, 2020). These possessions offer extraordinary potential to alternative to epoxy, bismaleimide, phenolics, and etc., in number of industrial applications. For example, conventional benzoxazines are worthy aspirants for fabrication of prepregs used for aerospace structure, and are presently applied regularly in the aerospace sectors. It is assessed that over the 30% weight reduction may be achieved with the used benzoxazine composites to replacing the metal, which consequences in reduction in the fuel consumption, and emissions.

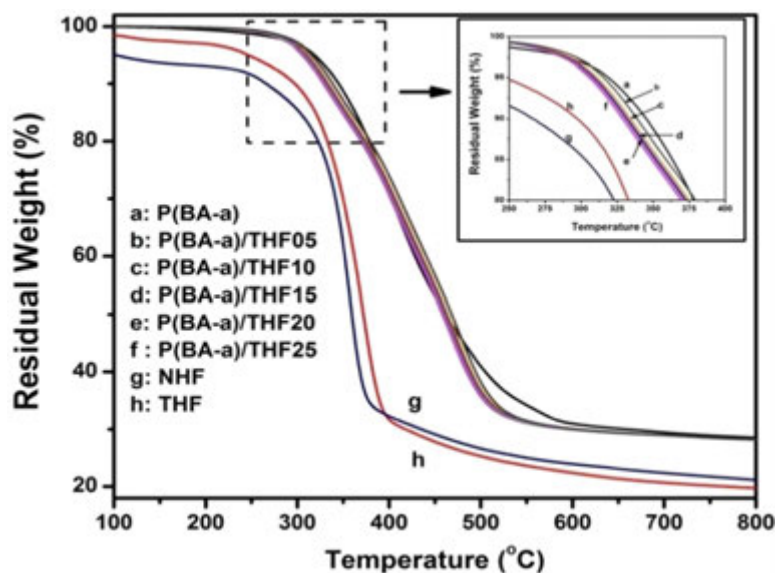


Fig. 21 TGA thermograms of fibers, neat PBZ and fiber reinforced PBZ composites. Copyright 2017, Reproduced with permission from Dayo, A.Q., Gao, B.-C., Wang, J., *et al.*, 2017. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. *Composites Science and Technology* 144, 114–124, from Elsevier.

Rimdusit group reported the development of aramid pulp/carbon fiber filled PBZ composites (Lertwassana *et al.*, 2019). They studied the possessions of carbon fibers and aramid pulps on thermal and mechanical properties, and tribological properties of composites are examined. The composites reveal higher thermal degradation and T_g temperatures, high friction coefficient, and better wear resistant. The developed PBZ composites might be useful as non-asbestos organic friction materials. From TGA (Fig. 19), the initial degradation T_{d5} % of PBZ composites raised with increasing the content of carbon fiber. Aramid pulp/carbon fiber filled PBZ composites with mass ratio of 100:0 (aramid pulp: carbon fiber) indicated the lower most T_{d5} % of 408°C increase of mass ratio of 0:100 exhibited the highest value of 437°C. It was noticed that the yield also improved with increase of the concentration of carbon fiber of the PBZ composites. The residual char values were in the range between 72.1% and 81.7% at 1000°C. Carbon fibers exhibited the high decomposition temperature with insignificant weight loss up to 1000°C (Fig. 19). The values of T_g of the PBZ composites were observed as 240, 244, 247, 262, and 265°C for mass ratios of aramid pulp:carbon fiber 100:0, 75:25, 50:50, 25:75, and 0:100, respectively. T_g values are elevated with increase in weight content of CFs. CFs might significantly constrain the movement of PBZ networks owing to the rigidity of CFs. These thermal results advised that CFs could enhance thermal stability of the PBZ composites.

Fig. 20 illustrates the worn-out surfaces of various weight ratio of carbon fiber: aramid pulp reinforced PBZ composites. Flaws and minor grooves were perceived on the surface of worn-out (Fig. 20(A)), inferring abrasive mechanism. In addition, small cracks were also perceived on PBZ composites surfaces after the introduction of CFs. Cracks and small grooves were decreased when CFs ratio increased in PBZ composites, prominent to improved wear resistance. Wear debris of PBZ composites were also studied to assess the tribological behavior by SEM and the results obtained are presented in Fig. 20. From SEM analysis, it was mostly observed plate shaped wear debris for all CFs reinforced PBZ composites. Certain spherical wear debris were also perceived only with aramid pulps reinforced PBZ composites. Carbon fiber/aramid pulp introduced PBZ composites might be possibly realistic as better performing friction materials.

Wang *et al.* reported the 5% NaOH (THF) activated hemp fibers reinforced bisphenol A-aniline based PBZ (PBA-a) by resin-fiber-resin composites (Dayo *et al.*, 2017). The effects of change in volume of fiber on the curing, thermal, thermo-mechanical and morphological properties of the PBZ composites were studied by DSC, DMA, TGA, and SEM. The results indicated that the NaOH treated hemp fiber reduce the curing temperature of benzoxazine, and increase the adhesion between matrix and fiber. From DSC curing, all hemp fiber reinforced BA-a blends showed lower initial exothermic peaks (T_i) and onset temperatures (T_p) when compared to that of neat BA-a monomer matrix. The T_i and T_p values were decreased to 177 and 230°C (hemp fiber from 0 to 25 vol%) from 213 and 246°C (neat BA-a), respectively. This reduction in the cure temperatures is due to the presence of -OH functional group on the hemp fiber, which act as catalyst to start the ring-opening polymerization at lower temperature. Further, it was also observed that the values of decomposition temperatures T_5 % (318–307°C) and T_{10} % (345–338°C) and residual char yields (28.5 to 28.0) of all hemp fiber reinforced PBZ composites (Fig. 21 and Table 2) were insignificantly affected with introduction of hemp fiber.

The SEM technique was used to assess the surface and fracture morphology of treated and untreated hemp fiber, and compatibility of fiber with PBA-a. From SEM (Fig. 22), better adhesion was perceived between fiber and matrix as increases of fiber fraction. Minor cavities were noticed on the fractured surfaces apparently owing to the deprivation of cellulosic and hemicelluloses

Table 2 Thermal properties of various filler reinforced polybenzoxazine matrix composites

Composites	T_g	Thermal Degradation			Weight Loss (%)	Reference
		IDT	($T_{10}\%$)	T_{max}		
PBA-a	169	318	345		28.5	Dayo <i>et al.</i> (2017)
PBA-a/THF05	175	315	338		28.2	Dayo <i>et al.</i> (2017)
PBA-a/THF10	177	314	337		28.1	Dayo <i>et al.</i> (2017)
PBA-a/-THF15	180	311	334		28.0	Dayo <i>et al.</i> (2017)
PBA-a/-THF20	181	309	332		28.1	Dayo <i>et al.</i> (2017)
PBA-a/-THF25	184	307	330		28.1	Dayo <i>et al.</i> (2017)
PBA-a	181	338	365		28.7	Dayo <i>et al.</i> (2018)
PBA-a/WHF	195	313	337		28.2	Dayo <i>et al.</i> (2018)
PBA-a/AHF	211	321	342		28.3	Dayo <i>et al.</i> (2018)
PBA-a/SHF	214	324	346		28.5	Dayo <i>et al.</i> (2018)
PP-a		396	465		38	Oliveira <i>et al.</i> (2020)
PBA-a		338	377		34	Oliveira <i>et al.</i> (2020)
BC(MS/P-a)	118	289	325		34	Oliveira <i>et al.</i> (2020)
BC(MS/BP-a)	135	288	327		29	Oliveira <i>et al.</i> (2020)
CE/BOZ	243	338	355		27.0	Zegaoui <i>et al.</i> (2018)
CE/BOZ/TNHF5-5	246	341	357		27.1	Zegaoui <i>et al.</i> (2018)
CE/BOZ/TNHF5-10	251	343	359		27.0	Zegaoui <i>et al.</i> (2018)
CE/BOZ/TNHF5-15	257	347	364		27.1	Zegaoui <i>et al.</i> (2018)
CE/BOZ/TNHF5-20	268	350	367		27.2	Zegaoui <i>et al.</i> (2018)
PBF-a		265	380		0	Wolter <i>et al.</i> (2020)
GFRP		359	496		71	Wolter <i>et al.</i> (2020)
BFRP		355	501		70	Wolter <i>et al.</i> (2020)
CFRP		262	467		27	Wolter <i>et al.</i> (2020)
CBz	129	304	347	444	12	Krishnadevi <i>et al.</i> (2020)
CBz/FRHA-1%	131	307	354	446	18	Krishnadevi <i>et al.</i> (2020)
CBz/FRHA-5%	133	314	357	457	32	Krishnadevi <i>et al.</i> (2020)
CBz/FRHA-10%	136	316	359	460	36	Krishnadevi <i>et al.</i> (2020)
CBz/FRHA-15%	141	317	363	464	40	Krishnadevi <i>et al.</i> (2020)
CBz/FRHA-20%	145	319	370	470	47	Krishnadevi <i>et al.</i> (2020)
PBA-a	169	315	338		29	Ramdani <i>et al.</i> (2014)
PBA-a/SN05	191	329	351		33	Ramdani <i>et al.</i> (2014)
PBA-a/SN10	195	341	375		41	Ramdani <i>et al.</i> (2014)
PBA-a/SN15	193	249	387		45	Ramdani <i>et al.</i> (2014)
PBA-a/SN20	201	360	393		52	Ramdani <i>et al.</i> (2014)
PBA-a/SN30	216	362	394		56	Ramdani <i>et al.</i> (2014)
PBZ/EP	171	264	337		21.0	Selvi <i>et al.</i> (2014b)
1.0% PBZ/EP/POSS	178	265	330		25.5	Selvi <i>et al.</i> (2014b)
3.0% PBZ/EP/POSS	183	267	331		29.8	Selvi <i>et al.</i> (2014b)
5.0% PBZ/EP/POSS	192	267	333		34.2	Selvi <i>et al.</i> (2014b)
PBZ-co-CPL	162	218			25.4	Selvi <i>et al.</i> (2014a)
0.5% PBZ-co-CPL/PZT	170	230			28.3	Selvi <i>et al.</i> (2014a)
1.0% PBZ-co-CPL/PZT	181	236			29.9	Selvi <i>et al.</i> (2014a)
1.5% PBZ-co-CPL/PZT	192	243			34.8	Selvi <i>et al.</i> (2014a)

components in the fiber surface during curing. The fracture surfaces exhibited the discreet gaps between matrix resin and fiber. Pull-out the fibers from the polymer matrix was found lower loading, causing the failure to test. However the fibers pull-out cavities also were diminished by increasing the weight content of fiber. These images afford exceptional explanation for the composites to support the data of mechanical properties.

The same research group reported the effect of alkali, cyclohexane/ethanol, and silane treatment of hemp fibers and their corresponding PBZ composites and studied the thermal, mechanical and morphological properties (Dayo *et al.*, 2018). From the studies lignin and hemicellulose in the fibers was removed after treated with cyclohexane/ethanol and alkali. The silane treatment enhanced the thermal properties of composites. The thermal stability of the composites was analyzed using TGA and are presented in Table 2 and Fig. 23. From the TGA thermogram, the $T_5\%$, $T_{10}\%$, decomposition temperatures and residual char was observed as 338°C, 365°C and 28.7%, respectively for neat poly(BA-a) matrix. In case of silane treated PBZ composites showed slightly lower $T_5\%$, $T_{10}\%$, decomposition temperatures and residual char values of 324°C, 346°C and 28.5% respectively. The thermal stability behavior of composite systems is lower than that of PBZ matrix. It was also noticed from thermal stability results that the thermal decomposition of the fiber reinforced PBZ composites can be reduced by the silane usage up to certain extent.

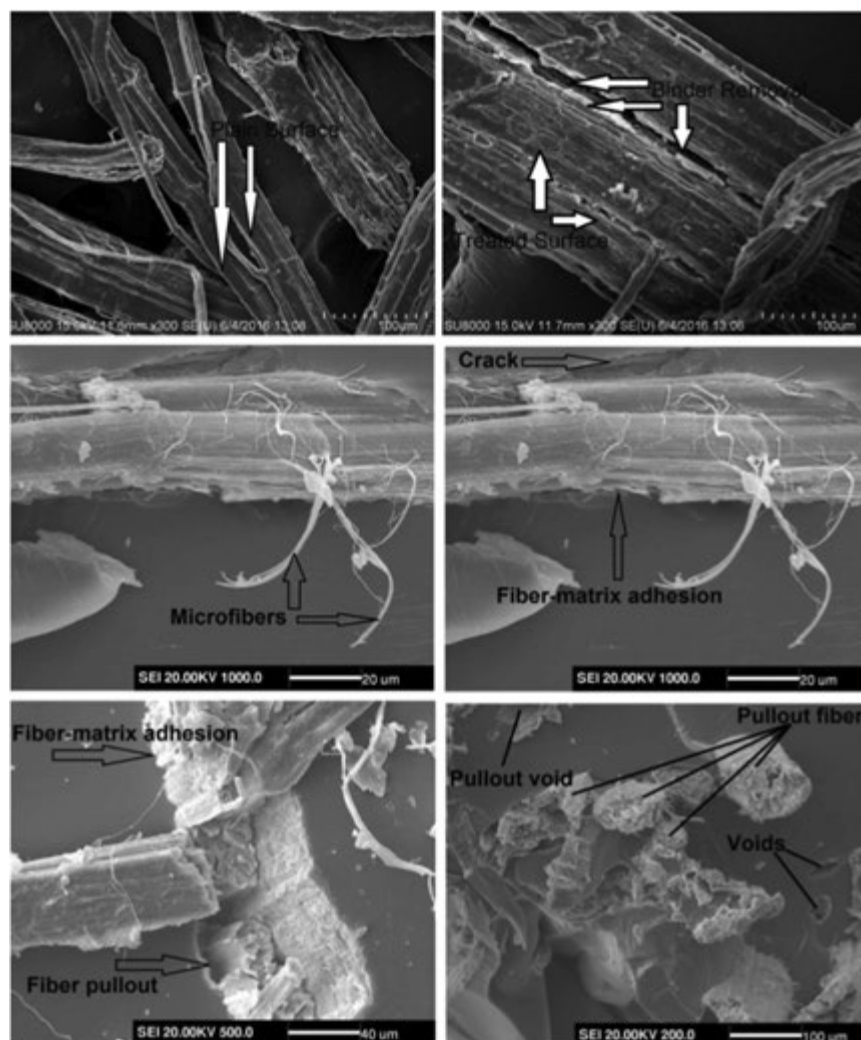


Fig. 22 SEM micrographs of the native hemp fiber, treated hemp fiber, fractured surface of PBA-a/THF. Copyright 2017, Reproduced with permission from Dayo, A.Q., Gao, B.-C., Wang, J., *et al.*, 2017. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. Composites Science and Technology 144, 114–124, from Elsevier.

The surface morphology of PBZ composites was studied with SEM and the results obtained are presented in Fig. 24. From the Fig. 24, neat PBZ perceived smooth surface endorses the brittle behavior of the PBZ. The fiber reinforced PBA-a/WHF composites showed numbers of cavities and fiber ruptures. These cavities are built-up on the fiber slip during rupturing, designating the smooth and glassy fiber surface. Further, the similar surface morphology was also observed for PBA-a/AHF composites. Further, the PBA-a/SHF composites, pull out fiber was completely roofed with the PBZ resin; this inferred that the treated silane fiber composites had efficient fiber and matrix interaction than the treated other composites. These outcomes are in good agreement with the formerly discussed efficacy coefficient for the SHF fiber PBZ composites.

Lomonaco research group developed the PBZ based bio-composites using natural fabrics of *Manicaria sacifera* (MS) (palm tree) and two BZ matrices prepared from bisphenol-A (BA-a) and phenol (*p*-a) (Oliveira *et al.*, 2020). They developed the bio-composites as bi-directional base treated fabrics reinforced with BZ resins (prepregs) and then polymerized in hot-press technique. The better compatibility of the BZ matrix with fabric was checked by SEM, which infers that base treated fabric attaining enhanced interfacial interaction. Thermal characterization results indicate the bio-based materials revealed excellent flame resistant properties. The $T_5\%$, $T_{10}\%$ decomposition temperatures and residual char values were slightly decreased for PBZ composites when compared to those of neat PBZ (Table 2 and Fig. 25). This slight reduction may be due to inherent nature of bio-fiber than the highly stable PBZ matrix. Though, the LOI values of bio-composites showed 29.1 and 31.1 of [BC(MS/BA-a)] and [BC(MS/P-a)], respectively, proved that the developed bio-composites from renewable feed-stocks qualifies for competent flame retardancy materials.

SEM technique was performed to check the surface fractured morphology of [BC(MS/BA-a)] and [BC(MS/P-a)] and are presented in Fig. 26. From SEM images, it was perceived that the fractured surface of BC(MS/P-a) indicates in a more organized

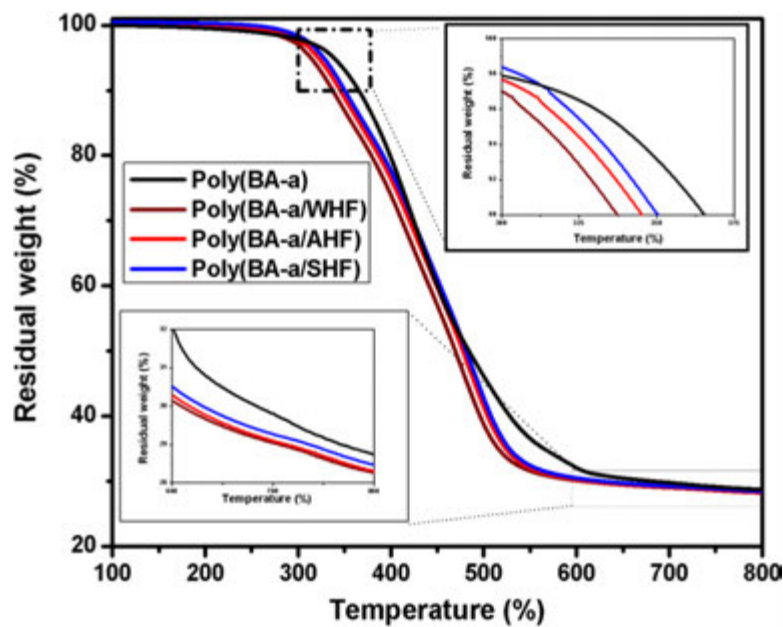


Fig. 23 TGA thermogram of the different treated hemp fiber reinforced PBZ composites. Copyright 2018, Reproduced with permission from Dayo, A.Q., Zegaoui, A., Nizamani, A.A., *et al.*, 2018. The influence of different chemical treatments on the hemp fiber/polybenzoxazine based green composites: Mechanical, thermal and water absorption properties. Materials Chemistry and Physics 217, 270–277, from Elsevier.

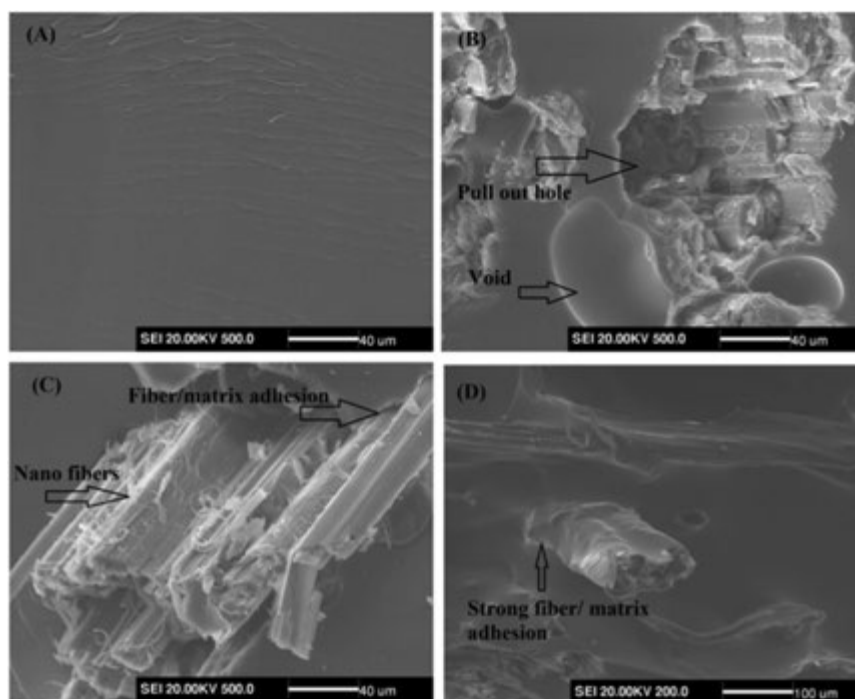


Fig. 24 The SEM images of (A). neat PBA-a matrix, and hemp fiber reinforced PBZ composites (B). PBA-a/WHF, (C). PBA-a/AHF and (D). PBA-a/SHF. Copyright 2018, Reproduced with permission from Dayo, A.Q., Zegaoui, A., Nizamani, A.A., *et al.*, 2018. The influence of different chemical treatments on the hemp fiber/polybenzoxazine based green composites: Mechanical, thermal and water absorption properties. Materials Chemistry and Physics 217, 270–277, from Elsevier.

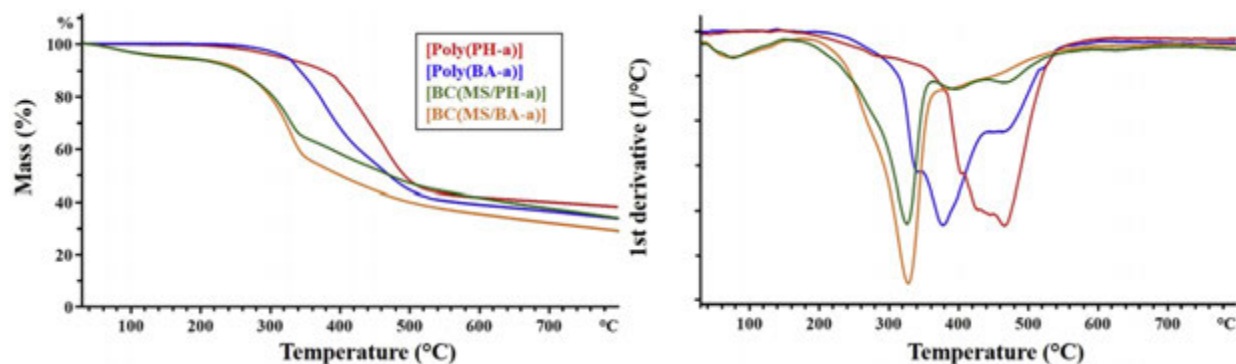


Fig. 25 TGA and DTG thermogram of neat PBZ matrix and bio-composites. Copyright 2020, Reproduced with permission from Oliveira, J.R., Kotzebue, L.R.V., Freitas, D.B., *et al.*, 2020. Towards novel high-performance bio-composites: Polybenzoxazine-based matrix reinforced with *Manicariassaccifera* fabrics. Composites Part B: Engineering 194 (1–10), 108060, from Elsevier.

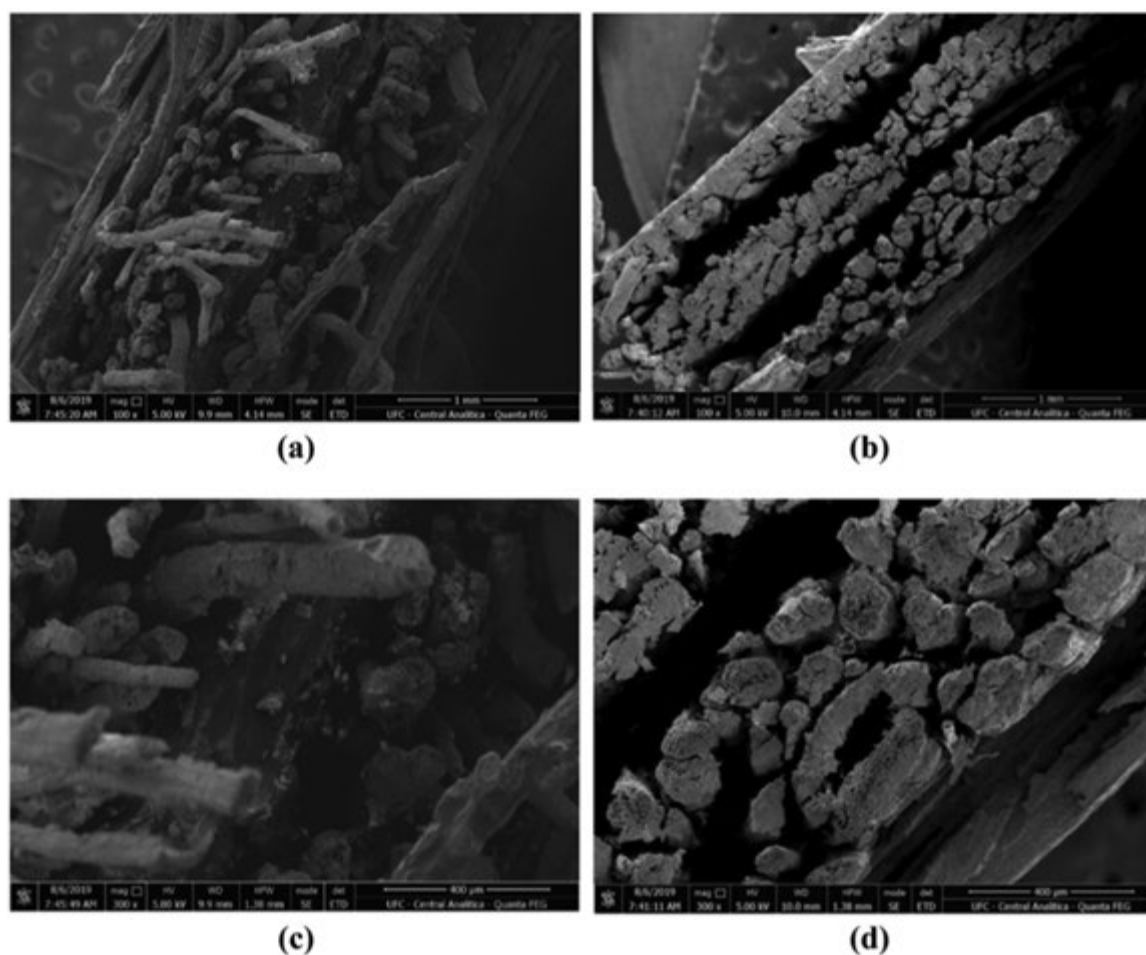


Fig. 26 SEM micrographs of fractured surfaces of BC(MS/BA-a) and BC(MS/P-a) bio-composites at diverse magnification (a) BC(MS/BA-a) (100 X), (b) BC(MS/P-a) (100X), (c) BC(MS/BA-a) (300X), and (d) BC(MS/P-a) (300X). Copyright 2020, Reproduced with permission from Oliveira, J.R., Kotzebue, L.R.V., Freitas, D.B., *et al.*, 2020. Towards novel high-performance bio-composites: Polybenzoxazine-based matrix reinforced with *Manicariassaccifera* fabrics. Composites Part B: Engineering 194 (1–10), 108060, from Elsevier.

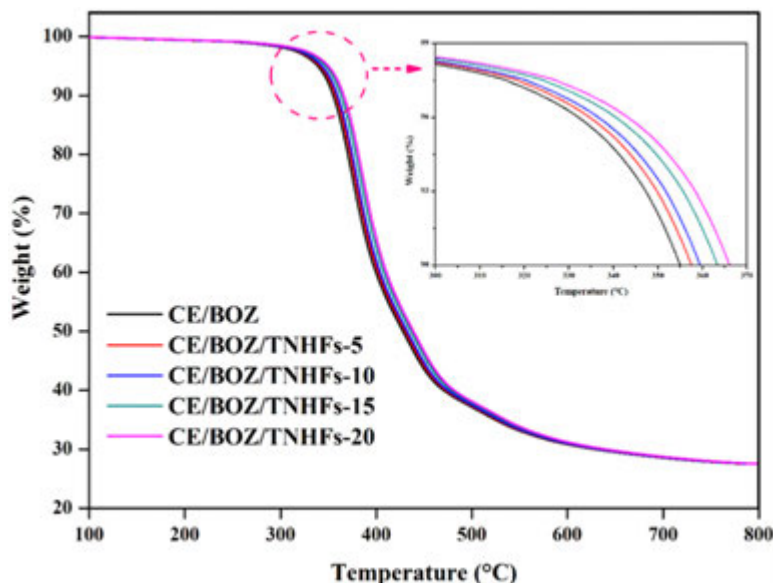


Fig. 27 TGA thermogram of neat CE/BOZ and various weight percentages TNHF filled loadings CE/BOZ/TNHF composites under N_2 atmosphere. Copyright 2018, Reproduced with permission from Zegaoui, A., Ma, R., Dayo, A.Q., *et al.*, 2018. Morphological, mechanical and thermal properties of cyanate ester/benzoxazine resin composites reinforced by silane treated natural hemp fibers. Chinese Journal of Chemical Engineering 26, 1219–1228, from Elsevier.

manner while, BC(MS/BA-a) shows the more uneven fiber pull-out from the matrix surface. Further, it was also observed that there was no phase separation (aggregation) between the matrix and fiber, indicating the firm and efficient adhesion in the interface region.

Wang research group reported the different weight concentration of silane treated natural hemp fiber (TNHP) filled cyanate ester/benzoxazine composites and studied their thermal and mechanical performance (Zegaoui *et al.*, 2018). Thermal properties of composites were studied with TGA and DSC analysis. From DSC results, it was noticed that the TNHP fiber reinforced CE/BOZ composites showed higher T_g values than those of neat CE/BOZ matrix. The values of T_g are improved with increasing the weight content of TNHP in the CE/BOZ composites. The T_g value was increased to 268°C (for 20% TNHP filled CE/BOZ composites) from 243°C for neat CE/BOZ. From TGA (Fig. 27), it was observed that the thermal performance was somewhat increased by introducing more and more TNHFs reinforcement in the CE/PBZ. The $T_5\%$, $T_{10\%}$ and residual char values were progressively improved from 341°C, 357°C and 27.1% for the CE/BOZ/TNHF-5 to 350°C, 367°C and 27.2% respectively for the maximum loaded TNHF in the CE/BOZ/TNHF-20. Such a regular increase in the thermal stability may be owing to the increasing high heat resistant behavior of TNHFs in the composites, which could reasonably increase the thermal properties of the composites by preventing the emission of volatile decomposition products, fragments and residual char formation.

In order to assess the interfacial adhesion between the CE/BOZ matrix and fiber, SEM images were accomplished to perceive the surface fractured morphology of neat CE/BOZ and its related composites and the results obtained are presented in Fig. 28. For neat CE/BOZ matrix, it was observed that smooth and glassy surfaces as well as regular river lines due to the high brittle behavior. In contrast, the composites showed small cavities and bubbles on the ruptured surfaces, which may be due to the concurrent degradation of hemicellulose and cellulose present in the fiber. It was also observed that the good bonding sites were developed between the fibers and CE/BOZ matrix as the fiber content increased. These SEM images also ascertain the outstanding mechanical performance achieved upon reinforcing varying amounts of TNHFs within the CE/BOZ matrix. Thus, the good thermal and mechanical performances observed for CE/BOZ blend composites suggested a potential application in the arena of construction, furniture, shipping and household products.

Koschek *et al.* reported the basalt fiber, glass fiber and carbon fiber filled PBZ composites using bisphenol-F/aniline based benzoxazine monomer (Wolter *et al.*, 2020). The FRPs displayed a uniform morphology with fully impregnated fibers and almost no porosity. CFs reinforced PBZ composites possess higher mechanical properties. Though, concerning the FST properties, glass and basalt reinforced PBZ outperformed CFs reinforced PBZ. To assess the impact of the different types of fiber filled PBZ composites on the thermal and thermo-oxidative stability was checked with TGA under nitrogen and ambient atmospheres condition and the results obtained are presented in Fig. 29 and Table 2. From TGA results, it was inferred that the inclusion of fiber reinforcement in to PBZ, the 2% and 10% mass loss degradation temperatures and residual char are increased. Mainly, the existence of fiber introduction reduced the quantity of polymer matrix that can decompose during thermal treatment. Moreover, GFRP and BFRP provide higher residual char than that of CFRP. For BFRP and GFRP char residue restored up-to 70%–71%, however CFRP char yield reduced 27 wt%. Mineral fiber filled PBF-a as showed higher thermal and thermal-oxidative stability than

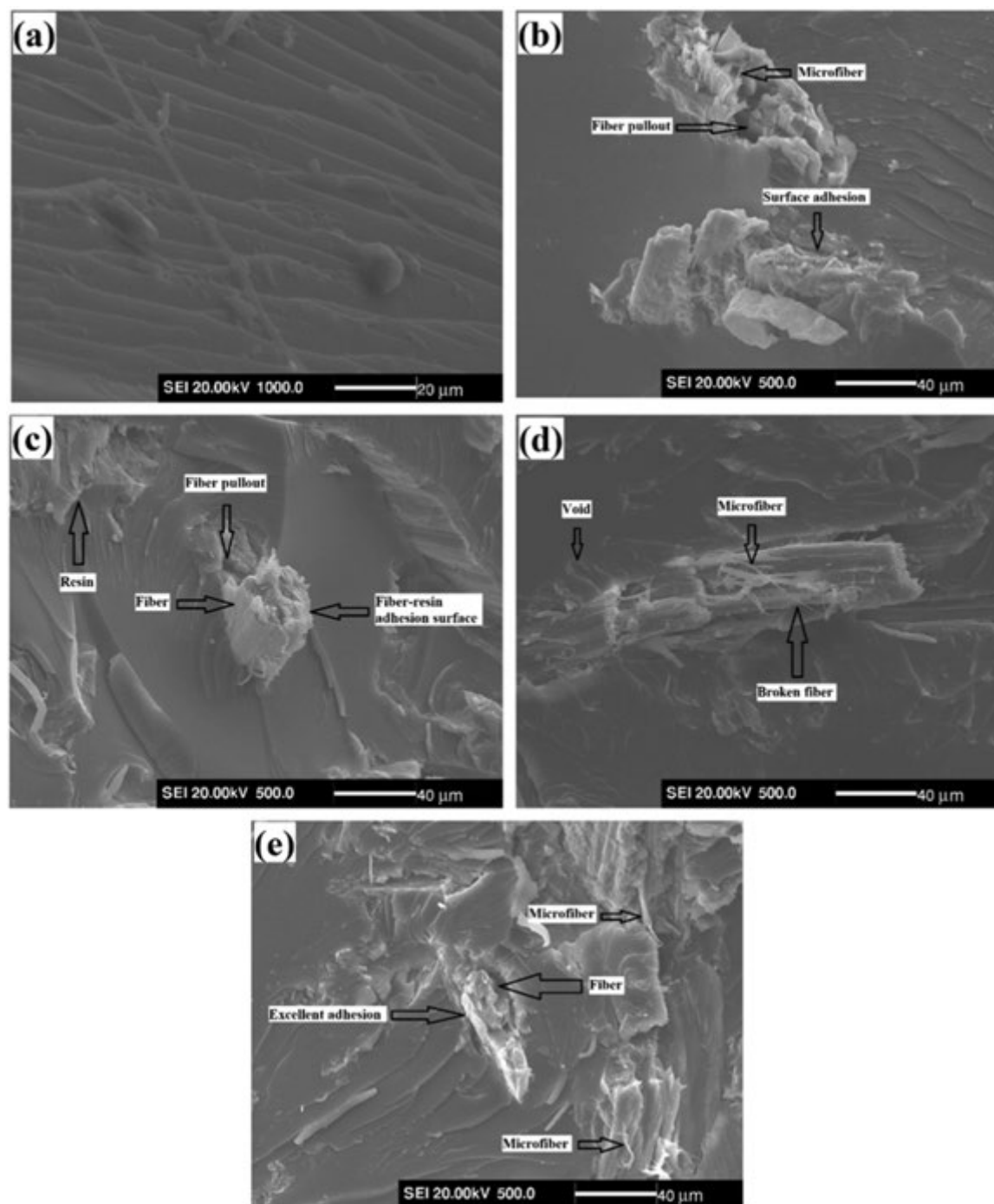


Fig. 28 SEM microgram of neat CE/PBZ and various weight percentages TNHF loaded CE/PBZ/TNHF composites. Copyright 2018, Reproduced with permission from Zegaoui, A., Ma, R., Dayo, A.Q., *et al.*, 2018. Morphological, mechanical and thermal properties of cyanate ester/benzoxazine resin composites reinforced by silane treated natural hemp fibers. Chinese Journal of Chemical Engineering 26, 1219–1228, from Elsevier.

those of CFs filled PBF-a. From SEM (**Fig. 30**) analysis, it was observed that all the FRP composites showed the uniform/homogeneous morphology with well-penetrated fibers with almost zero cavity.

Krishnadevi *et al.* reported the cardanol based PBZ bio-composites using functionalized rice husk ash (FRHA) and cardanol based benzoxazine monomer (CBz) via thermal ring opening polymerization and studied their thermal, electrical, and biological properties (Krishnadevi *et al.*, 2020). The thermal stability of neat CBz matrix, and different weight content of FRHA reinforced CBz bio-composites were studied using TGA and the results obtained are presented in **Fig. 31** and **Table 2**. The $T_5\%$ and $T_{10}\%$ weight loss degradation temperature obtained are 304–319°C and 347–370°C, respectively, for FRHA-filled CBz bio-composites.

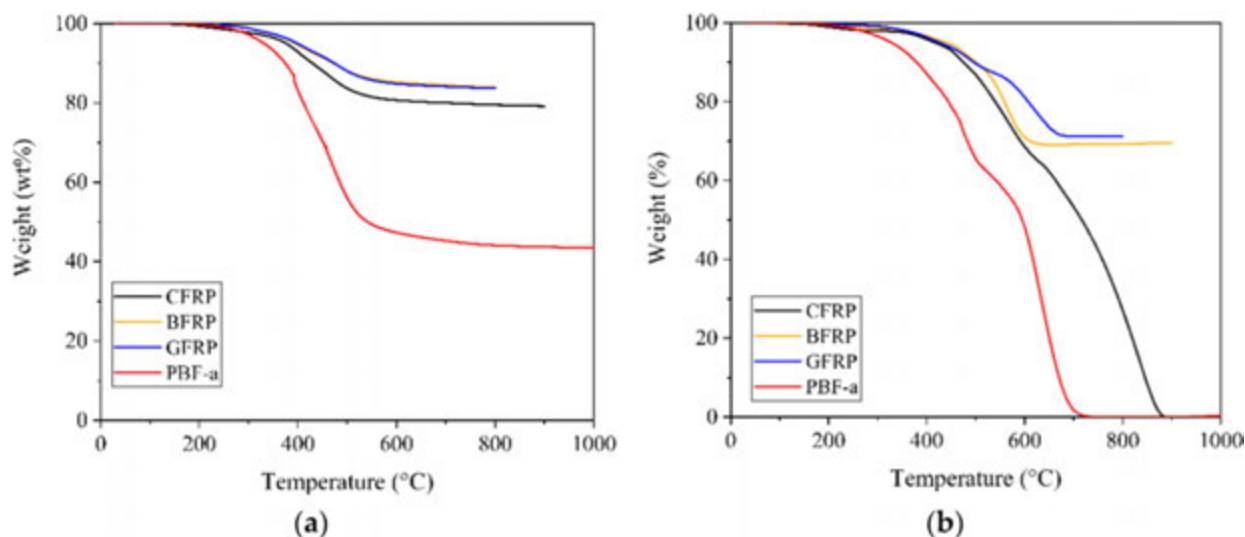


Fig. 29 TGA thermogram of neat PBF-a and carbon, glass and basalt fiber reinforced PBF-a under (a) nitrogen and (b) ambient atmospheres. Copyright 2020, Reproduced with permission from Wolter, N., Beber, V.C., Sandinge, A., *et al.*, 2020. Carbon, glass and basalt fiber reinforced polybenzoxazine: The effects of fiber reinforcement on mechanical, fire, smoke and toxicity properties. *Polymers* 2020 (12), 2379, from MDPI.

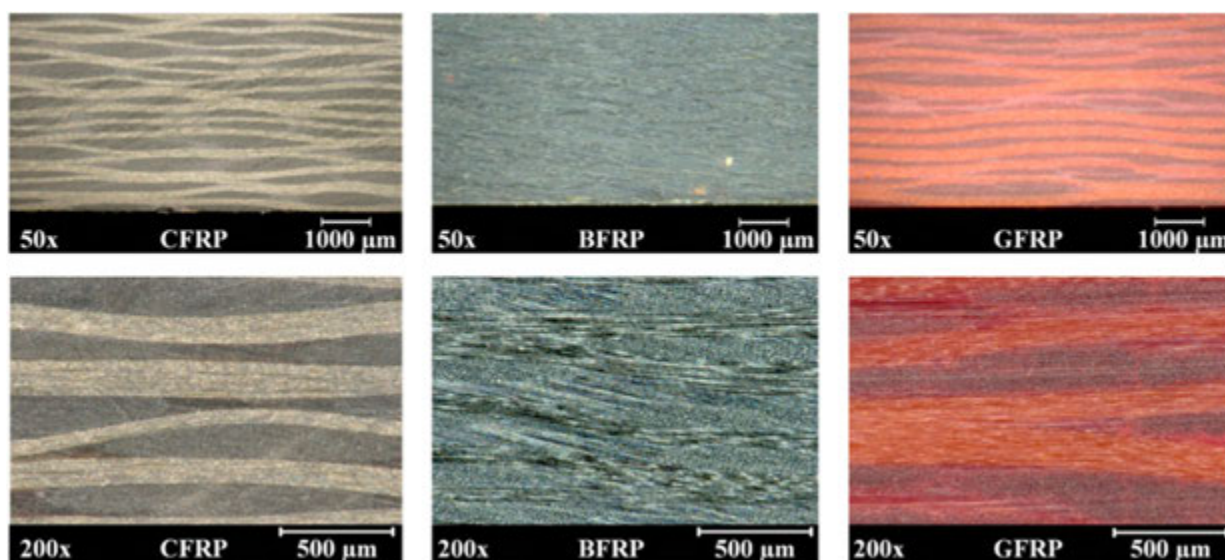


Fig. 30 SEM images of cross-sections of carbon, glass and basalt fiber reinforced PBF-a with the magnifications of 50X and 200X. Copyright 2020, Reproduced with permission from Wolter, N., Beber, V.C., Sandinge, A., *et al.*, 2020. Carbon, glass and basalt fiber reinforced polybenzoxazine: The effects of fiber reinforcement on mechanical, fire, smoke and toxicity properties. *Polymers* 2020 (12), 2379, from MDPI.

The residual char yield increased significantly to 47% for FRHA-filled CBz bio-composites from 12% for neat CBz. This may be due to the inert silica layer of FRHA, which act as the passive protective layer on surface of the CBz bio-composites, and in turn, inhibits the further degradation. Further, the value of T_g are also increased to 145°C for CBz bio-composites from 129°C for neat CBz.

Liu *et al.* reported the preparation of varying weight percentage concentration (0–30 wt%) of silicon nitride (SN) filled PBZ composites via a compression molding (Ramdani *et al.*, 2014). The TGA results shown that the thermal stability of these PBZ composites was greatly enhanced by the introduction of SN filler. Fig. 32 and Table 2 display the TGA results of neat PBA-a and different SN reinforced PBZ composites. As it is evidently observed, the 5 and 10 wt% decomposition temperatures of neat PBA-a are 315 and 338°C, respectively, with the residual char value of 29%. In case of 5 and 10 wt% SN reinforced PBz composites, the decomposition temperatures and char yield values were observed as 329–362°C, 351–394°C and 33%–56% respectively. The introduction of SN nanoparticles into PBA-a matrix ominously enhanced its thermal stability which increased with increasing the percentage weight content of SN reinforcement. This enhancement in thermal properties is owing to the influencing impact of nano-SN in the PBZ that behave as the thermal insulator to protect the PBA-a matrix. The value of T_g of neat PBZ matrix and SN

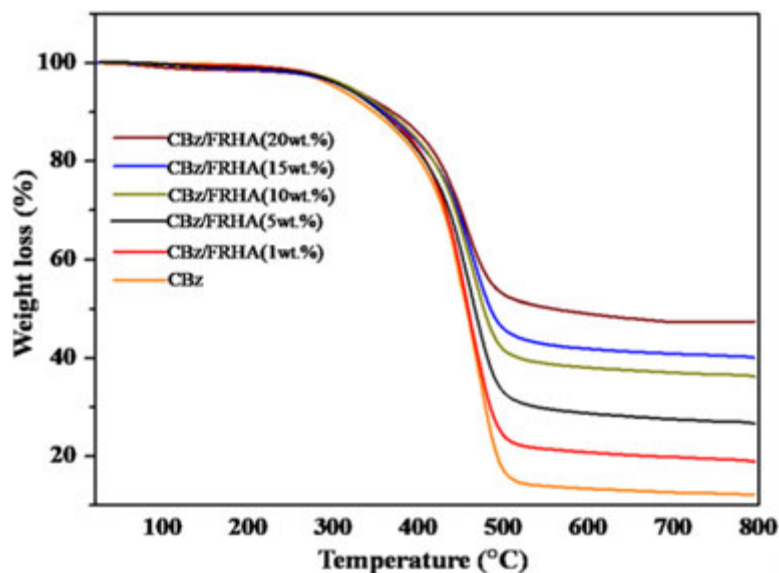


Fig. 31 TGA thermogram of neat CBz and CBz/FRHA reinforced composites. Copyright 2020, Reproduced from Krishnadevi, K., Devaraju, S., Sriharshitha, S., Alagar, M., Priya, Y.K., 2020. Environmentally sustainable rice husk ash reinforced cardanol based polybenzoxazine bio-composites for insulation applications. *Polymer Bulletin* 77, 2501–2520 by permission of Springer.

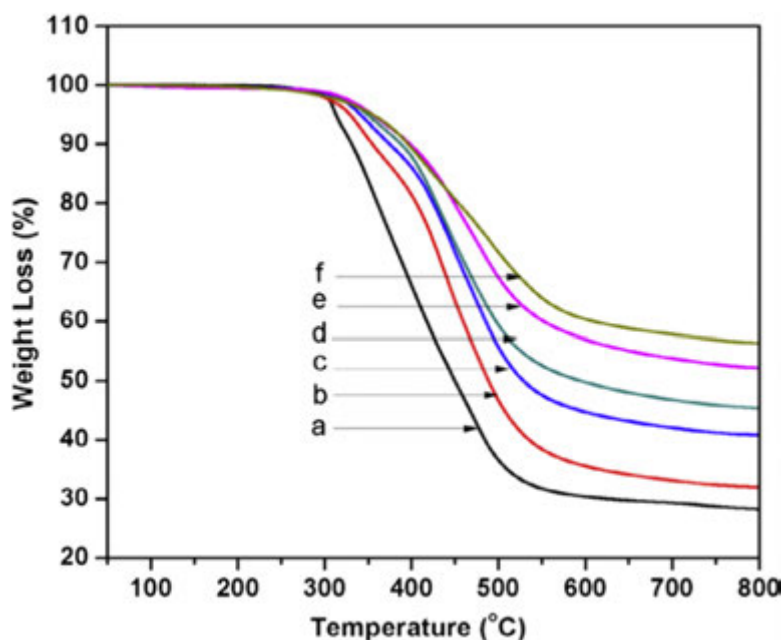


Fig. 32 TGA thermogram of neat PBA-a and PBA-a/SN nanocomposites at various SN weight percentage: (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 30%. Copyright 2014, Reproduced with permission from Ramdani, N., Wang, J., Wang, H., *et al.*, 2014. Mechanical and thermal properties of silicon nitride reinforced polybenzoxazine nanocomposites. *Composites Science and Technology* 105, 73–79, from Elsevier.

filled PBZ composites were checked with DMA and the results obtained are depicted in **Fig. 33** and **Table 2**. From the DMA studies, the value of T_g was increased with increasing the weight percentages of SN in to the PBZ. The improvement in T_g was ascribed to the increase of cross-linking density and rigidity. Fractured surface morphology of neat PBA-a and SN reinforced PBA-a composites are studied with SEM analysis and the results are shown in **Fig. 34**. From SEM micrographs, it is clearly realized that the neat PBA-a shows a smooth and unremarkable fractured surface morphology that indicated its brittle in nature. Though, the morphology of its composites at different weight percentage of SN (**Fig. 34(B–F)**) possesses the good and homogeneous dispersion of SN filler in the PBA-a matrix with improved interfacial interaction.

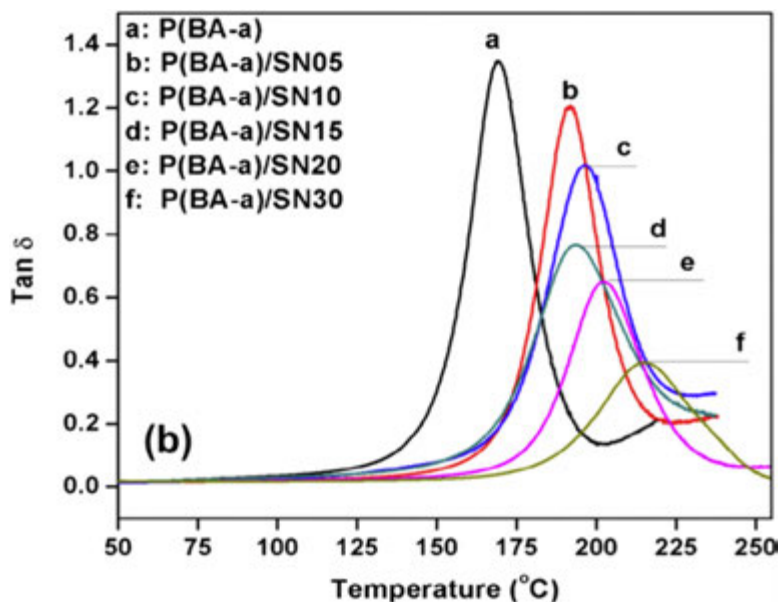


Fig. 33 T_g values (Tan δ) from DMA thermogram of neat PBA-a and PBA-a/SN nanocomposites. Copyright 2014, Reproduced with permission from Ramdani, N., Wang, J., Wang, H., *et al.*, 2014. Mechanical and thermal properties of silicon nitride reinforced polybenzoxazine nanocomposites. *Composites Science and Technology* 105, 73–79, from Elsevier.

Alagar research group reported the effect of UV resistant material based on PBz as polymer matrix and variable weight content of (0, 1.0, 3.0, and 5.0 wt%) POSS as filler (Selvi *et al.*, 2014b). The PBZ/EP matrix and composites developed were analyzed using diverse analytical techniques. The values of T_g of OG-POSS introduced PBZ/EP nano-composites are enhanced with increasing the weight content of OG-POSS. Fig. 35 shows the TGA graph of PBZ/EP/POSS composites, the introduction of small amount of OG-POSS (1.0, 3.0 and 5.0 wt%) into the PBZ/EP, there is no considerable enhancement was perceived in the value of $T_5\%$ and $T_{10\%}$ weight loss temperature. While the residual char values is noticeably increased from 21 wt% (neat PBZ/EP) to 34.2 wt% (5 wt% of PBZ/EP/POSS). High residual char value is a valuable information to predict the behavior of flame retardance. This may be owing to the combined influences of higher amount of silica and aromatic groups improved the cross-link density and hinders the dissemination of fragments.

Fig. 36 displays the TEM image of 1.0, 3.0 and 5.0 wt% PBZ/EP/POSS nanocomposites. It can be observed that the OG-POSS materials are dispersed uniformly in the PBZ/EP matrix. No confined domains and no phase separation were perceived even at nanometer scale, suggesting that reinforcement POSS were uniformly dispersed throughout the matrix system and there is no POSS agglomerations has achieved. Data obtained from SEM and tensile studies indicate that the 5.0 wt% POSS filled PBZ/EP nanocomposites satisfy the requirements of UV resistant material.

The same research group reported the cyclophosphazene nanotube (PZT) reinforced poly(benzoxazine-co- ϵ -caprolactam) (P(BZ-co-CPL)) composites in order to enhance the thermal and flame retardant performances (Selvi *et al.*, 2014a). The UL-94 outcomes of P(BZ-co-CPL)/PZT hybrid nanocomposites exhibited V-1 rating, while the neat P(BZ-co-CPL) indicated burning rating. From thermal studies, it was observed that the PZT reinforced P(BZ-co-CPL) composites exhibited better T_g and thermal decomposition performance than those of neat P(BZ-co-CPL). The TEM images determine the homogeneous dispersion of PZT fiber in the (PBZ-co-CPL) matrix. The DSC analysis reveal that the T_g values of neat P(BZ-co-CPL) and PZT filled P(BZ-co-CPL) are 162, 170, 181 and 192°C respectively. The PZT filled P(BZ-co-CPL) composites possess higher T_g values than that of neat P(BZ-co-CPL). This might be owing to the PZT fiber in the P(BZ-co-CPL) rises the rigidity/steric interruption, and constrains the movement of polymer matrix. From the TGA (Fig. 37) analysis it was concluded that the initial $T_5\%$ loss temperatures are 218, 230, 236 and 243°C respectively for neat P(BZ-co-CPL) and PZT (0.5, 1.0, 1.5 wt%) filled P(BZ-co-CPL). The increase in the initial decomposition is owing to the PZT fiber present in the composite system which rises the steric hindrance and high crosslinking network. Similarly, the residual char yield values obtained are 19.8%, 27.2%, 31.0% and 34.8% respectively for neat and PZT filled PBZ/EP systems. The high char may be due to the higher thermally stable PZT fiber in the P(BZ-co-CPL) matrix. The morphology behavior of PZT fiber reinforced P(BZ-co-CPL)/PZT composites was studied with HR-TEM, and the corresponding TEM images are presented in Fig. 38. From TEM images, it was confirmed that PZT were mostly in the form of nanofiber and revealed a fine length dissemination. It was established that the PZT fibers are about 2–6 μ m in length, about 30–50 nm with inner diameter. Further, it can be noticed that PZT nanofibers are uniformly dispersed throughout P(BZ-co-CPL) matrix, which contributes to their good compatibility of PZT fiber and polymer matrix phase result in high thermal and mechanical performances.

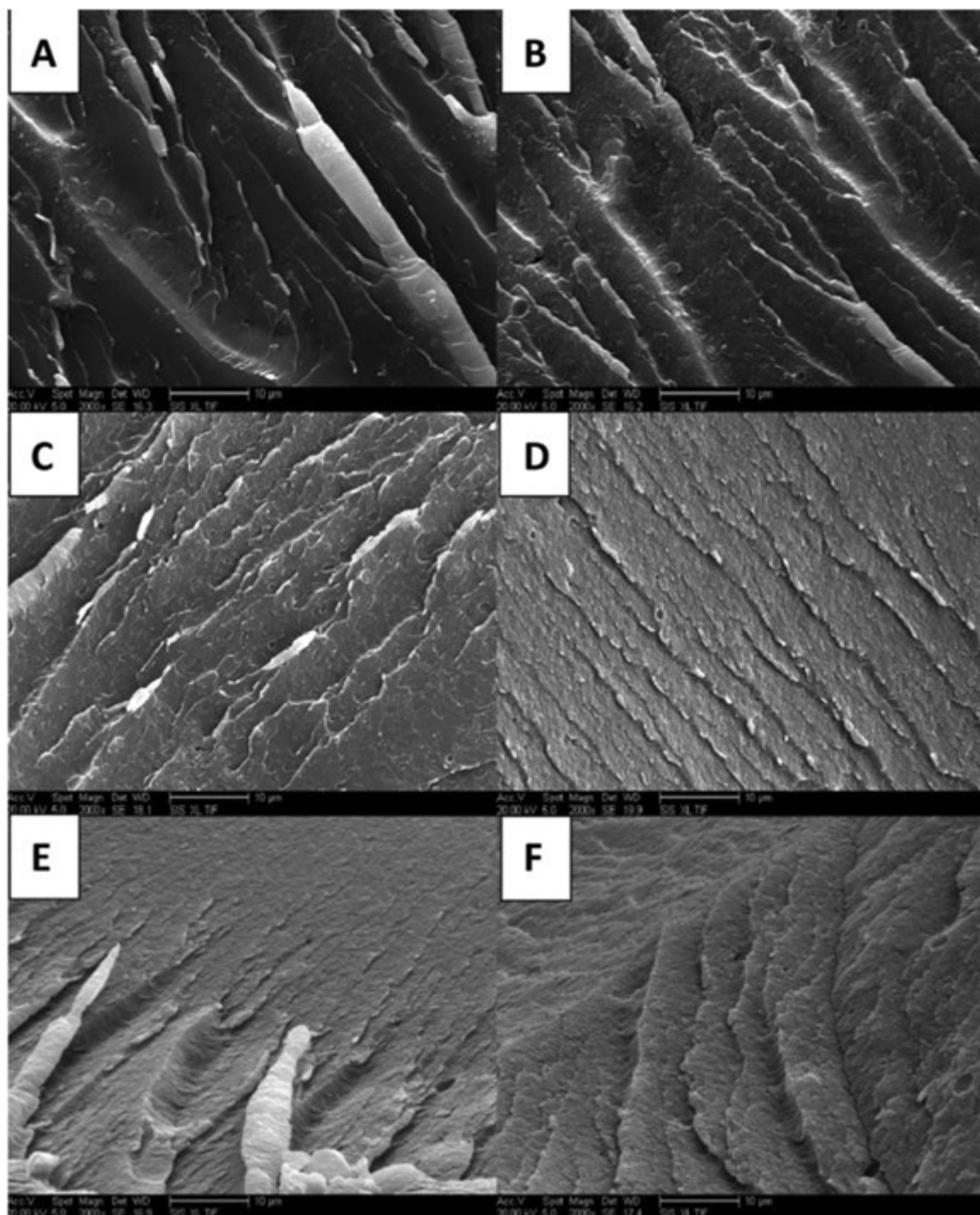


Fig. 34 SEM fractured morphology of neat PBA-a and PBA-a/SN nanocomposites at various SN weight percentage: (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 30%. Copyright 2014, Reproduced with permission from Ramdani, N., Wang, J., Wang, H., *et al.*, 2014. Mechanical and thermal properties of silicon nitride reinforced polybenzoxazine nanocomposites. *Composites Science and Technology* 105, 73–79, from Elsevier.

Summary

Polymer matrix composites are one of the most economical materials and are used in different fields together with marine, aerospace, construction, sports components, off-shore applications, fire and flame resistant components, waterlines, construction of building and etc., owing to their exceptional processability, lower weight, good crosslinking capability, and outstanding mechanical properties. In this article we discussed the thermal and morphological properties of various polymer matrix

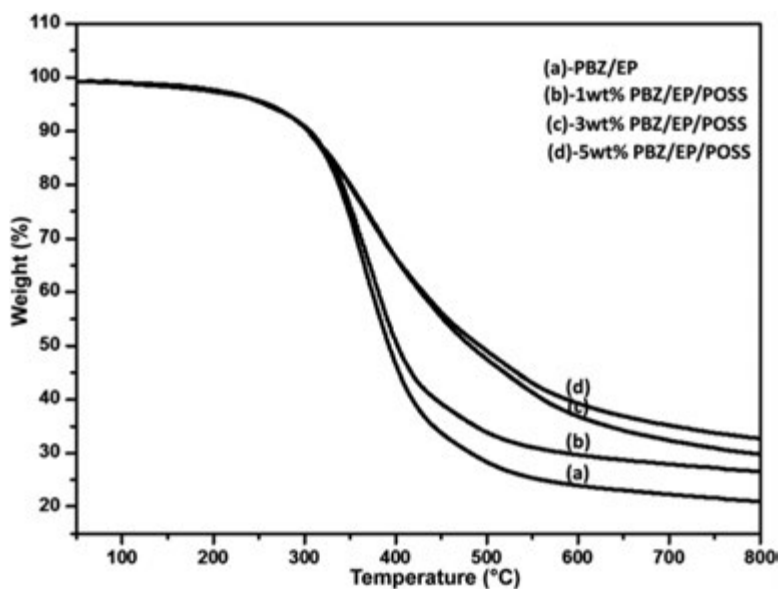


Fig. 35 TGA thermogram for neat PBZ/EP and PBZ/EP/POSS nanocomposites. Copyright 2014, Reproduced from Selvi, M., Devaraju, S., Vengatesan, M.R., *et al.*, 2014b. The effect of UV radiation on Polybenzoxazine/epoxy/OG-POSS nanocomposites. RSC Advances 4, 8238–8244 by permission of The Royal Society of Chemistry (RSC).

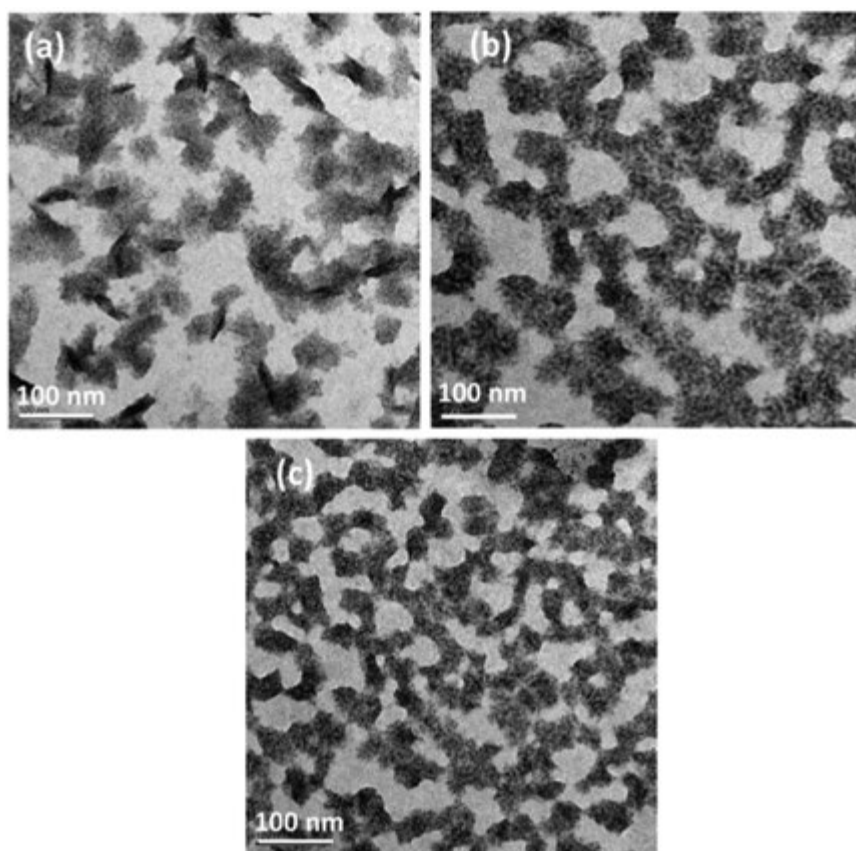


Fig. 36 TEM images of (a) 1.0, (b) 3.0 and (c) 5.0 wt% of PBZ/EP/POSS composites. Copyright 2014, Reproduced from Selvi, M., Devaraju, S., Vengatesan, M.R., *et al.*, 2014b. The effect of UV radiation on Polybenzoxazine/epoxy/OG-POSS nanocomposites. RSC Advances 4, 8238–8244 by permission of The Royal Society of Chemistry (RSC).

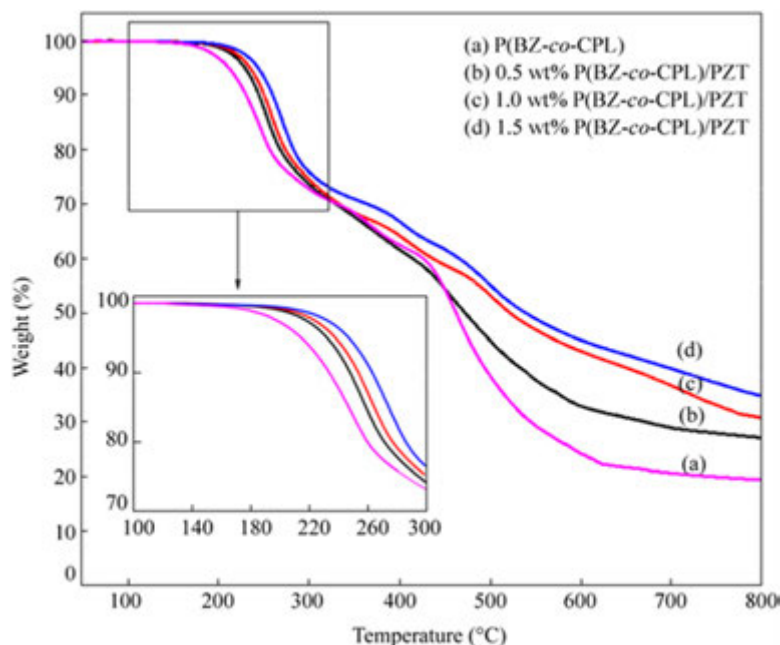


Fig. 37 TGA thermogram of neat P(BZ-co-CPL) and P(BZ-co-CPL)/PZT nanocomposites. Copyright 2014, Reproduced from Selvi, M., Devaraju, S., Sethuraman, K., Revathi, R., Alagar, M., 2014a. Cyclotriphosphazene fibre reinforced polybenzoxazine-co- ϵ -caprolactam nanocomposites for flame retardant applications. *Chinese Journal of Polymer Science* 32, 1086–1098 by permission of Springer.

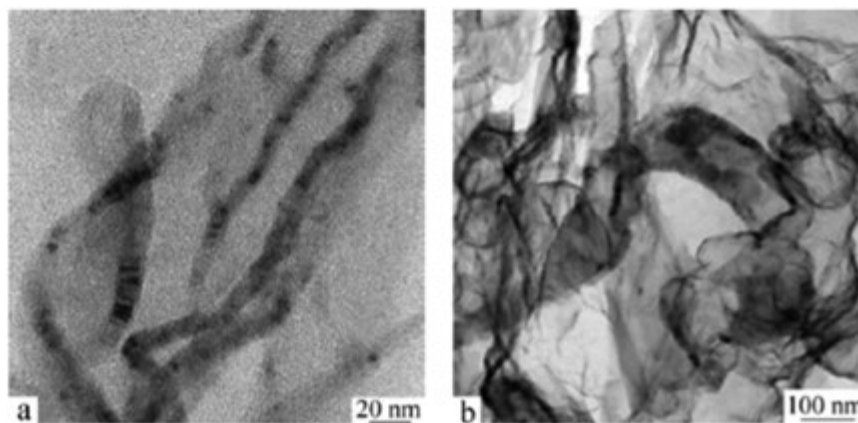


Fig. 38 HR-TEM images of (a) 0.5 wt% and (b) 1.0 wt% of P(BZ-co-CPL)/PZT nano-composites. Copyright 2014, Reproduced from Selvi, M., Devaraju, S., Sethuraman, K., Revathi, R., Alagar, M., 2014a. Cyclotriphosphazene fibre reinforced polybenzoxazine-co- ϵ -caprolactam nanocomposites for flame retardant applications. *Chinese Journal of Polymer Science* 32, 1086–1098 by permission of Springer.

composites especially epoxy matrix, polybenzoxazine matrix and different reinforcements namely glass fiber, natural hemp fiber, basalt fiber, carbon fiber, silicon nitride fiber, carbon nanotubes, PZT fibers, POSS and etc. The present article also discusses the possible applications of the polymer matrix composites. In the upcoming years, mainly in the aerospace and automotive, energy production and other related industries need cutting edge novel polymer composites for high performance, cost competitive processing methods including environmentally friendly fabrication methods. Hence, the emergent interest of the usage of renewable polymer matrices and reinforcement to improve the properties of polymer matrix composites are warranted for widespread range of industrial and engineering applications.

References

- Advani, S.G., Hsiao, K.T. (Eds.), 2012. *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*. UK: Woodhead Publishing.
- Alagar, M., Ashok Kumar, A., Mahesh, K.P.O., Dinakaran, K., 2000a. Studies on thermal and morphological characteristics of E-glass/Kevlar 49 reinforced siliconized epoxy composites. *European Polymer Journal* 36, 2449–2454.

- Alagar, M., Thanikaivelan, T.V., Ashok Kumar, A., 2000b. Mechanical properties of E-glass fibre reinforced siliconized epoxy polymer composites. *Polymer Composites* 21, 739–744.
- Alagar, M., Thanikaivelan, T.V., Ashok Kumar, A., Mohan, V., 1999. Synthesis and characterization of high performance polymeric hybrid siliconized epoxy composites for aerospace applications. *Materials and Manufacturing Processes* 14, 67–83.
- Allothman, O.Y., Jawaid, M., Senthilkumar, K., *et al.*, 2020. Thermal characterization of sate palm/epoxy composites with fillers from different parts of the tree. *Journal of Materials Research and Technology* 9, 15537–15546.
- Ashok Kumar, A., Alagar, M., Rao, R.M.V.G.K., 2002. Synthesis and characterization of siliconized epoxy-1,3-bis(maleimido)benzene intercrosslinked matrix materials. *Polymer* 43, 693–702.
- Babu, K., Balasubramanian, N., Ramesh, T., 2018. Role, effect, and influences of micro and nano-fillers on various properties of polymer matrix composites for microelectronics: A review. *Polymers Advanced Technologies* 29, 1568–1585.
- Barbero, E.J. (Ed.), 2017. *Introduction to Composite Materials Design*. UK: CRC Press.
- Benin, S.R., Kannan, S., Bright, R.J., Moses, A.J., 2020. A review on mechanical characterization of polymer matrix composites & its effects reinforced with various natural fibres. *Materials Today: Proceedings* 33, 798–805.
- Benzaït, Z., Trabzon, L.A., 2018. A review of recent research on materials used in polymer–matrix composites for body armor application. *Journal of Composite Materials* 52, 3241–3263.
- Bondzic, S., Hodgkin, J., Krstina, J., Mardel, J., 2006. Chemistry of thermal ageing in aerospace epoxy composites. *Journal of Applied Polymer Science* 100, 2210–2219.
- Chung, D.D.L., 2017. Processing-structure-property relationships of continuous carbon fiber polymer-matrix composites. *Materials Science and Engineering: R: Reports* 113, 1–29.
- Chandramohan, A., Dinkaran, K., Ashok Kumar, A., Alagar, M., 2012. Synthesis and characterization of epoxy modified cyanate ester POSS nanocomposites. *High Performance Polymers* 24, 405–417, from SAGE Publications.
- Ciesielski, M., Burk, B., Heinzmann, C., Döring, M., 2017. Fire-retardant high-performance epoxy-based materials. In: Wang, D.-Y. (Ed.), *Novel Fire Retardant Polymers and Composite Materials*. UK: Woodhead Publishing, pp. 3–51.
- Dayo, A.Q., Gao, B.-C., Wang, J., *et al.*, 2017. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. *Composites Science and Technology* 144, 114–124.
- Dayo, A.Q., Zegaoui, A., Nizamani, A.A., *et al.*, 2018. The influence of different chemical treatments on the hemp fiber/polybenzoxazine based green composites: Mechanical, thermal and water absorption properties. *Materials Chemistry and Physics* 217, 270–277.
- Devaraju, S., Alagar, M., 2018. Unsaturated polyester–macrocomposites. In: Thomas, S., Hosur, M., Chirayil, C.J. (Eds.), *Unsaturated Polyester Resins: Fundamentals, Design, Fabrication, and Applications*. UK: Elsevier.
- Devaraju, S., Krishnadevi, K., Naveena, E., Alagar, M., 2019a. Design and development of polybenzoxazine-POSS hybrid materials from renewable starting materials for low k and low surface free energy applications. *Materials Research Express* 6, 104007.
- Devaraju, S., Krishnadevi, K., Sriharshitha, S., Alagar, M., 2019b. Design and development of environmentally friendly polybenzoxazine–silica hybrid from renewable bio-resource. *Journal of Polymers and the Environment* 27, 141–147.
- Devaraju, S., Vengatesan, M.R., Selvi, M., Song, J.K., Alagar, M., 2013. Hyper branched polysiloxane-based diglycidyl ether of bisphenol a epoxy composite for low k dielectric application. *Polymer Composites* 34, 904–911.
- Dusek, K., 1985. *Epoxy Resins and Composites*. Switzerland: Springer.
- Esmizadeh, E., Naderi, G., Yousefi, A.A., Milone, C., 2016. Thermal and morphological study of epoxy matrix with chemical and physical hybrid of nanoclay/carbon nanotube. *JOM* 68, 362–373.
- Gan, P.G., Sam, S.T., bin Abdullah, M.F., Omar, M.F., 2020. Thermal properties of nanocellulose-reinforced composites: A review. *Journal of Applied Polymer Sciences* 137, 48544.
- Ghori, S.W., Siakeng, R., Rasheed, M., Saba, N., Jawaid, M., 2018. The role of advanced polymer materials in aerospace. In: Jawaid, M., Thariq, M. (Eds.), *Sustainable Composites for Aerospace Applications*. UK: Woodhead Publishing, pp. 19–34.
- Ghosh, N.N., Kiskan, B., Yagci, Y., 2007. Polybenzoxazines—New high performance thermosetting resins: Synthesis and properties. *Progress in Polymer Sciences* 32, 1344–1391.
- Hamerton, I., Kratz, J., 2018. The use of thermosets in modern aerospace applications. In: Guo, Q. (Ed.), *Thermosets Structure, Properties, and Applications*, second ed. UK: Elsevier, pp. 303–340.
- Hull, D., Clyne, T.W. (Eds.), 1996. *An Introduction to Composite Materials*, second ed. Cambridge University Press.
- Hussain, F., Hojjati, M., 2006. Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview. *Journal of Composite Materials* 40, 1511–1575.
- Ishida, H., Froimowicz, P. (Eds.), 2017. *Advanced and Emerging Polybenzoxazine Science and Technology*. UK: John Fedor Publisher, Elsevier.
- Ishida, H., Agag, T. (Eds.), 2017. *Handbook of Benzoxazine Resins*. UK: Elsevier.
- Iuliana, E., Sorina, B., Gărea, A., Iovu, H., 2019. Developing polybenzoxazine composites based on various carbon structures. *Macromolecular Chemistry and Physics* 220, 1800322.
- Jamrozik, A., Barczewski, M., Framski, G., *et al.*, 2020. Synthesis and characterization of low-cost cresol-based benzoxazine resins as potential binders in abrasive composites. *Materials* 13, 2995.
- Jose, J.P., Joseph, K., 2012. Advances in polymer composites: Macro- and microcomposites – State of the art, new challenges, and opportunities. In: Thomas, S., Joseph, K., Malhotra, S.K., Goda, K., Sreekala, M.S. (Eds.), *Polymer Composites*, first ed., 1. Germany: Wiley.
- Kanimozhi, K., Devaraju, S., Vengatesan, M.R., Selvaraj, V., Alagar, M., 2013. Studies on synthesis and characterization of surface-modified mullite fibre-reinforced epoxy nanocomposites. *High Performance Polymers* 25, 658–667.
- Karvanis, K., Rusnáková, S., Krejčí, O., Žaludek, M., 2020. Preparation, thermal analysis, and mechanical properties of basalt fiber/epoxy composites. *Polymers* 12, 1785.
- Kavimani, V., Prakash, K.S., Thankachan, T., Udayakumar, R., 2020. Synergistic improvement of epoxy derived polymer composites reinforced with graphene oxide (GO) plus titanium di oxide (TiO₂). *Composites Part B: Engineering* 191, 107911.
- Kiskan, B., 2018. Adapting benzoxazine chemistry for unconventional applications. *Reactive and Functional Polymers* 129, 76–88.
- Krishnadevi, K., Devaraju, S., Sriharshitha, S., Alagar, M., 2019. Development and characterization of fully bio-based polybenzoxazine-silica hybrid composites for low-k and flame-retardant applications. *Polymers for Advanced Technologies* 30, 1856–1864.
- Krishnadevi, K., Devaraju, S., Sriharshitha, S., Alagar, M., Priya, Y.K., 2020. Environmentally sustainable rice husk ash reinforced cardanol based polybenzoxazine bio-composites for insulation applications. *Polymer Bulletin* 77, 2501–2520.
- Kuan, C.-F., Chen, W.-J., Li, Y.-L., *et al.*, 2010. Flame retardance and thermal stability of carbon nano-tube epoxy composites prepared from sol–gel method. *Journal of Physics and Chemistry of Solids* 71, 539–543.
- Kumar, A., Sharma, K., Dixit, A.R., 2020. Carbon nanotube- and graphene-reinforced multiphase polymeric composites: Review on their properties and applications. *Journal of Materials Science* 55, 2682–2724.
- Lertwassana, W., Parnklang, T., Mora, P., Jubsilp, C., Rimdusit, S., 2019. High performance aramid pulp/carbon fiber-reinforced polybenzoxazine composites as friction materials. *Composites Part B: Engineering* 177 (1–10), 107280.
- Lyu, Y., Ishida, H., 2019. Natural-sourced benzoxazine resins, homopolymers, blends and composites: A review of their synthesis, manufacturing and applications. *Progress in Polymer Science* 99, 101168.

- Mahato, K.K., Dutta, K., Ray, B.C., 2019. Assessment of mechanical, thermal and morphological behavior of nano- Al_2O_3 embedded glass fiber/epoxy composites at in-situ elevated temperatures. *Composites Part B: Engineering* 166, 688–700.
- Mahesh, V., Joladarashi, S., Kulkarni, S.M., 2020. A comprehensive review on material selection for polymer matrix composites subjected to impact load. *Defence Technology* 17, 257–277. doi:10.1016/j.dt.2020.04.002.
- Mangalgi, P., 1999. Composite materials for aerospace applications. *Bulletin of Materials Science* 22, 657–664.
- Matykievicz, D., 2020a. Biochar as an effective filler of carbon fiber reinforced bio-epoxy composites. *Processes* 8 (724), 1–13.
- Matykievicz, D., 2020b. Hybrid epoxy composites with both powder and fiber filler: A review of mechanical and thermomechanical properties. *Materials* 13, 1802.
- Mittal, V., Saini, R., Sinha, S., 2016. Natural fiber-mediated epoxy composites – A review. *Composites Part B: Engineering* 99, 425–435.
- Mostafa, N.H., Ismarrubie, Z.N., Sapuan, S.M., Sultan, M.T.H., 2017. Fibre prestressed polymer-matrix composites: A review. *Journal of Composite Materials* 51, 39–66.
- Nagendiran, S., Hamerton, I., Alagar, M., 2010. Octasilsesquioxane-reinforced DGEBA and TGDDM epoxy nanocomposites: Characterization of thermal, dielectric and morphological properties. *Acta Materialia* 58, 3345–3356.
- Njuguna, J. (Ed.), 2016. *Lightweight Composite Structures in Transport: Design, Manufacturing, Analysis and Performance*. UK: Woodhead Publishing, Elsevier.
- Njuguna, J., Pielichowski, K., 2003. Polymer nanocomposites for aerospace applications: Properties. *Advanced Engineering Materials* 5, 769–778.
- Oliveira, J.R., Kotzebue, L.R.V., Freitas, D.B., *et al.*, 2020. Towards novel high-performance bio-composites: Polybenzoxazine-based matrix reinforced with *Manicaria saccharifera* fabrics. *Composites Part B: Engineering* 194 (1–10), 108060.
- Parikh, H.H., Gohil, P.P., 2015. Tribology of fiber reinforced polymer matrix composites – A review. *Journal of Reinforced Plastics and Composites* 34, 1340–1346.
- Quilter, A., 2001. *Composites in Aerospace Applications*. USA: IHS, (IHS White Paper).
- Rajak, D.K., Pagar, D.D., Menezes, P.L., Linul, E., 2019. Fiber-reinforced polymer composites: Manufacturing, properties, and applications. *Polymers* 11 (1667), 1–37.
- Ramdani, N., 2017. *Properties Enhancement of Reinforced Polybenzoxazine Composites*. Paris: LAP LAMBERT Academic Publishing.
- Ramdani, N., Wang, J., Wang, H., *et al.*, 2014. Mechanical and thermal properties of silicon nitride reinforced polybenzoxazine nanocomposites. *Composites Science and Technology* 105, 73–79.
- Rana, S., Figueiro, R. (Eds.), 2016. *Advanced Composite Materials for Aerospace Engineering Processing, Properties and Applications*. UK: Woodhead Publishing.
- Ratna, D., Karger-Kocsis, J., 2008. Recent advances in shape memory polymers and composites: A review. *Journal of Materials Science and Technology* 43, 254–269.
- Santhosh Kumar, K.S., Reghunadhan Nair, C.P., 2010. *Polybenzoxazines: Chemistry and Properties*. USA: SmithersRapra Technology.
- Sapiai, N., Jumahat, A., Jawaid, M., Midani, M., Khan, A., 2020. Tensile and flexural properties of silica nanoparticles modified unidirectional Kenaf and hybrid glass/Kenaf epoxy composites. *Polymers* 12, 2733.
- Sarawut, R., Chanchira, J., Sunan, T., 2013. *Alloys and Composites of Polybenzoxazines*. Springer.
- Saxena, D., Maiti, P., 2020. Polymer composites in aerospace applications. In: Pawar, S. (Ed.), *Progress and Prospects in Nanoscience Today*. New York: Nova Science Publishers, pp. 59–76.
- Selvi, M., Devaraju, S., Sethuraman, K., Revathi, R., Alagar, M., 2014a. Cyclotriphosphazene fibre reinforced polybenzoxazine-co-v-caprolactam nanocomposites for flame retardant applications. *Chinese Journal of Polymer Science* 32, 1086–1098.
- Selvi, M., Devaraju, S., Vengatesan, M.R., *et al.*, 2014b. The effect of UV radiation on Polybenzoxazine/epoxy/OG-POSS nanocomposites. *RSC Advances* 4, 8238–8244.
- Selvi, M., Devaraju, S., Alagar, M., 2019a. Cyclotriphosphazene nanofiber-reinforced polybenzoxazine/epoxy nanocomposites for low dielectric and flame-retardant applications. *Polymer Bulletin* 76, 3785–3801.
- Selvi, M., Devaraju, S., Venkatesan, M.R., Alagar, M., 2019b. Synthesis and characterization of heterocyclic core-based polybenzoxazine matrices. *Journal of Applied Polymer Sciences* 136, 47134.
- Sethuraman, K., Prabunathan, P., Alagar, M., 2014. Thermo-mechanical and surface properties of POSS reinforced structurally different diamines cured epoxy nanocomposites. *RSC Advances* 4, 45433–45441.
- Shalin, R.E. (Ed.), 1995. *Polymer Matrix Composites*. UK: Chapman and Hall.
- Soutis, C., 2005. Fibre reinforced composites in aircraft construction. *Progress in Aerospace Sciences* 41, 143–151.
- Sreenivasulu, B., Ramji, B.R., Nagaral, M., 2018. A review on graphene reinforced polymer matrix composites. *Materials Today: Proceedings* 5, 2419–2428.
- Suchitra, M., Renukappa, N.M., 2016. The thermal properties of glass fiber reinforced epoxy composites with and without fillers. *Macromolecular Symposia* 361, 117–122.
- Thomas, S., Joseph, K., Malhotra, S.K., Goda, K., Sreekala, M.S. (Eds.), 2012. *Polymer Composites: Volume 1 Macro and Microcomposites*, first ed. Germany: Wiley.
- Thoppul, S.D., Finegan, J., Gibson, R.F., 2009. Mechanics of mechanically fastened joints in polymer–matrix composite structures – A review. *Composites Science and Technology* 69, 301–329.
- Tikhani, F., Moghari, S., Jouyandeh, *et al.*, 2020. Curing kinetics and thermal stability of epoxy composites containing newly obtained nano-scale aluminum hypophosphite (AlPO_2). *Polymers* 12, 644.
- Toldy, A., Szolnoki, B., Marosi, G.Y., 2011. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. *Polymer Degradation and Stability* 96, 371–376.
- Vengatesan, M.R., Devaraju, S., Alagar, M., 2011. Studies on thermal, mechanical and morphological properties of organoclay filled azomethine modified epoxy nanocomposites. *High Performance Polymer* 23, 3–10.
- Vijay Kumar, V., Balaganesan, G., Lee, J.K.Y., *et al.*, 2019. A Review of recent advances in nano engineered polymer composites. *Polymers* 11 (644), 1–20.
- Wanasinghe, D., Aslani, F., Ma, G., Habibi, D., 2020. Review of polymer composites with diverse nanofillers for electromagnetic interference shielding. *Nanomaterials* 10, 541.
- Wang, R.-M., Zheng, S.-R., Zheng, Y.-P. (Eds.), 2011. *Polymer Matrix Composites and Technology*. UK: Woodhead Publishing, Elsevier.
- Wang, X., Jiang, M., Zhou, Z., Gou, J., Hui, D., 2017. 3D printing of polymer matrix composites: A review and prospective. *Composites Part B: Engineering* 110, 442–458.
- Wolter, N., Beber, V.C., Sandinge, A., *et al.*, 2020. Carbon, glass and basalt fiber reinforced polybenzoxazine: The effects of fiber reinforcement on mechanical, fire, smoke and toxicity properties. *Polymers* 2020 (12), 2379.
- Yasmin, A., Daniel, I.M., 2004. Mechanical and thermal properties of graphite platelet/epoxy composites. *Polymer* 45, 8211–8219.
- Zegaoui, A., Ma, R., Dayo, A.Q., *et al.*, 2018. Morphological, mechanical and thermal properties of cyanate ester/benzoxazine resin composites reinforced by silane treated natural hemp fibers. *Chinese Journal of Chemical Engineering* 26, 1219–1228.

A New Design of Epoxy Based Composites Reinforced With Devulcanized Rubber, Alumina Fiber and BN

Alaeddin B Irez, CentraleSupélec, University Paris-Saclay, Gif-sur-Yvette, France and University Paris-Saclay, Gif-sur-Yvette, France
Emin Bayraktar, Supmeca-Paris, School of Mechanical and Manufacturing Engineering, Saint-Ouen, France
Ibrahim Miskioglu, Michigan Technological University ME-EM Department, Houghton, MI, United States

© 2018 Elsevier Inc. All rights reserved.

This is a reproduction of Alaeddin B. Irez, Emin Bayraktar, Ibrahim Miskioglu, A New Design of Epoxy Based Composites Reinforced With Devulcanized Rubber, Alumina Fiber and BN, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2018, doi:[10.1016/B978-0-12-803581-8.11328-1](https://doi.org/10.1016/B978-0-12-803581-8.11328-1).

Introduction

In the last decade, by the breakthrough advances in technology, single materials have some difficulties to respond the high expectations of the industry. For this reason, material manufacturers are investigating novel multifunctional materials. In this regard, composite materials offer various possibilities in many different applications. In particular, polymer matrix composites help to the investigators in achieving the asked properties in the existence of proper fillers.

Recently, high thermal conductive composites have a prominent place in microelectronics industry because of miniaturization and increasing power demands. Therefore, generated heat during the operation must be dissipated effectively from the device to maintain the reliability and lifespan [1]. Thanks to its low cost, outstanding electrical insulation property and ease of processing, epoxy resin is an optimal moulding compound for encapsulating heat-dissipating electronic devices. However, heat dissipation capability of epoxy resin should be improved by adding high thermal conductive fillers [2]. Various studies have been realized by altering type of fillers including metal particles (iron, zinc and copper) and ceramic particles (boron nitride (BN), alumina (Al_2O_3), silicon carbide (SiC) and aluminium nitride (AlN)). There are some drawbacks of metallic fillers compared to ceramics such as high density and susceptibility to oxidation. For ceramic particles, BN and AlN are very effective due to their high thermal conductivity. Nevertheless, AlN is affected easily from the moisture whereas BN does not have this disadvantage [3–5]. For this reason, in this study BN and alumina have been used due to their favourable mechanical and thermal properties. As the second reinforcement, alumina has good thermal conductivity, inertness to most acids and alkalis, high adsorption capacity, thermal stability and electrical insulation, and so on. Also, it is inexpensive, non-toxic and highly abrasive [6–8]. More specifically, in this study alumina has been used in fiber form and it has advantages compared to particle form. For instance, the diameter of alumina fiber is about two times larger than that of carbon fiber. Also, another beneficial parameter as interfacial strength and elastic modulus in a radial direction (Young's modulus of alumina fiber is much larger than that of carbon fiber in a radial direction) may also contribute to the strength and fracture mechanisms [9]. Besides, alumina fibers have outstanding compressive strength and shear properties [10].

Although the use of BN to improve thermal conductivity is quite common, hybridization of the matrix with fresh scrap rubber introduces a novelty in this area. Also, rubber particles are thought a good option to reduce the brittleness of the matrix. In addition, the use of fresh scrap rubber adds a value to this study in terms of economic and environmental aspects. For instance, non-used vulcanized scrap rubber causes to costly landfills. Also, in the context of landfilling, due to the impermeability and shape of discarded tires, they hold water for a long while and this creates a habitat for mosquito larvae as well as other animals such as rodents and snakes [11,12]. These may carry infections namely malaria, cephalitis, dengue and chikungunya. Besides, if these piles burst into flames, it is quite difficult to extinguish them [13]. Last but not least, some additives of landfilled tires such as colorants, stabilizers, flame retardants and plasticizers may leach from the bulk of the tires to the soil. Hence, they can harm or kill some beneficial bacterial colony in the soil [14]. For this reason, in this study by recycling of vulcanized rubbers we open a window into the green manufacturing of the multifunctional composites.

This work presents processing of recycled rubbers blended with epoxy resin to create novel composites in economic way. Main objective of this research is to determine the mechanical and physical properties of these composites. During this study, physical properties such as glass transition temperature and phase transitions are determined with dynamical mechanical analysis (DMA) and differential scanning calorimeter (DSC). Then, bending tests are realized with smooth specimens. After that, nano indentation tests are examined to see the time dependent behaviour and wear characteristics. In addition, surface hardness is determined by means of Shore D hardness measurement and macro wear characteristics are evaluated by means of scratch test. At the end, fracture surfaces are observed by means of scanning electron microscopy (SEM) to study the toughening and damage mechanisms.

Experimental Conditions

Materials Processing

The use of recycled rubbers in a composite system is more complicated than general belief for various reasons. Due to the former vulcanization process, cross-linked structure of rubber limits the movement of rubber chains and restrain the interaction forces between epoxy matrix and scrap rubber particles. For this reason, a decrease in the performance of final product is observed

[15–17]. In this case, in order to improve materials properties of the final product, devulcanization operation is recommended. According to ASTM definition, devulcanization is “a combination of depolymerization, oxidation and increased plasticity” since during reclamation each of these processes generally occurs. *In fact*, the reverse of the vulcanization can be named as devulcanization [18]. During sulphur vulcanization, C–S and S–S bonds are generated. On the other hand, in an ideal devulcanization process, it is expected only C–S and S–S bonds cleavage without any degradation on the main-chain. Devulcanization occurs if the provided energy is higher than the link energies of monosulfidic C–S (270 kJ/mol) and polysulfidic S–S (240 kJ/mol) bonds without exceeding that of peroxide C–C (345 kJ/mol) bonds. In the frame of the present work, the energy for devulcanization is provided by microwaves and it is followed by chemical surface treatments. This combined method contains exposing recycled rubbers to microwave heating in a short time followed by a pre-chemical treatment that is applied in practical point of view. By this way, a good cohesion is supplied at the interface between epoxy resin and rubber powders to improve the properties of the recycled rubber (SBR with a particle size varying from 30 to 130 μm) coming from the sportive equipment. It means that they are fresh, clean and completely different from ground tire.

First, recycled rubbers are exposed to short microwave heating during 4 min in order to avoid degradation of the main chains. Then, chemical treatment is applied. The principal of the chemical treatment consists in a short silanization process followed by acrylic acid and a small amount of toluene solution to activate the surface of the rubber particles. After drying of the chemical treated rubber powders, at the final stage, devulcanized rubbers are mixed with epoxy resin powders. This mixture is used as a matrix of the new composites then, the new designed composites are manufactured by using classical powder metallurgy methods. After the mixture of the reinforcements (BN, alumina fiber and SiC) in the matrix, milling process is carried out during 4 h.

Subsequent to having a homogeneous powder compound, the composite specimens are manufactured by using double uniaxial action press at a temperature of 180°C under a pressure of 70 MPa during the heating of 30 min. All of the specimens (30/50 mm in diameter) are cooled slowly in the press. All of the specimens are post-cured isothermally at 80°C for 24 h. This procedure is illustrated in Fig. 1.

The compositions designed for two types of the composites in this work (hereafter called as EBNA I-II-III) are given in Table 1.

Thermal Analyses and Physical Characterization

Differential scanning calorimeter (DSC) analyses are performed on DSC Q10N2 apparatus of TA Instruments, USA, from – 80 to 400°C in air flow with a 1 dm³/min flow rate and heating rate of 10°C/min.

Dynamic properties, storage modulus (E') and mechanical loss angle tangent ($\tan \delta$) of the epoxy based composites are investigated using a Dynamic Mechanical Thermal Analyser Q800 system (TA Instruments). The data are obtained at a frequency of 1 Hz, 0.1% strain in the temperature range from – 80 to 200°C using a heating rate of 3°C/min under single cantilever bending mode. The dimensions of the investigated samples are as follows: width 10 mm, length 30 mm, and the thickness 3 mm.

Microscopical Observation and Three Point Bending Testing

Microstructure and fracture surface damage analyses have been carried out by means of optical (OM) and scanning electron microscopy (SEM). SEM observation is realized on fracture surface of the tested specimens with Scope/JSM-6010LA Jeol® electron microscope.

After post curing, hardness measurements on the specimens are performed. Shore D hardness test measurements on the polished flat surfaces of the specimens are carried out according to ASTM D 2240 using Shore D hardness tester, (type HBD-100-0).

Three-point bending tests (3PB) have been carried out according to the ASTM D790 standards. Deflection of the specimen is measured by the crosshead position and crosshead speed is selected as 1 mm/min. Flexural strength and strain are obtained from the test results. The test specimen is placed to the Instron 5569 bending test machine's supports and force is applied until it breaks. At least three specimens for each composition are used and standard deviation and average values are given in results article with standard deviation values.

Nano-Indentation Analyses by Means of Creep and Wear Tests

Creep tests using a nano-indenter are performed on the two compositions manufactured to see the time dependent behaviour. On each sample 20 indents are performed on a 5 × 4 grid with a Berkovich indenter. The indents are spaced 50 μm along the 5-indent side and 75 μm along the 4-indent side. The load is increased at a rate of 1 mN/s to the max load and kept at the maximum load for 500 s then unloaded.

Scratch testing capability of a nano-indenter is utilized to perform relatively fast wear tests to compare the wear behaviour of the different samples. Wear tests are conducted by a conical tip with a 90° cone angle. Tests are run under a normal load of 20 mN applied over a linear track of 500 nm for 50 cycles.

Damage Analysis by Means of Scratch Test and 3D Optical Roughness Meter

Scratch tests results give a basic idea on the tribological behaviour of the epoxy and recycled elastomer-based composites designed in the current research. After the scratch test, damage zone is investigated by a 3D optical surface scanner to assess damage in terms of scratch depth and average scratch roughness.

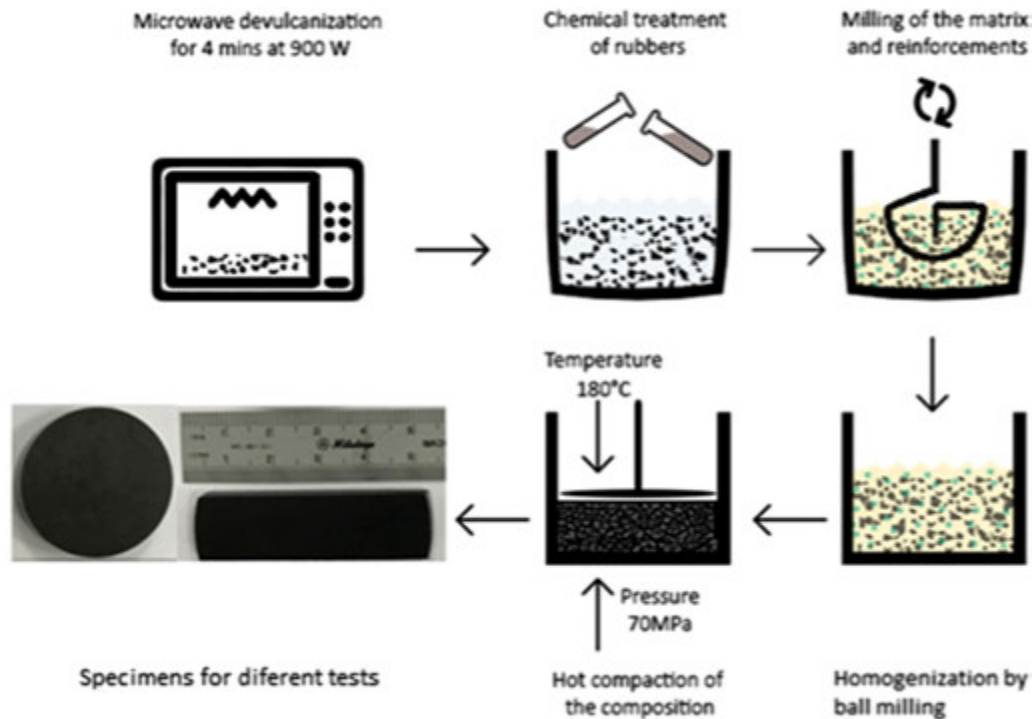


Fig. 1 Manufacturing of recycled rubber modified epoxy-based composites.

Table 1 Composition of the epoxy-rubber based composites

<i>Epoxy-Rubber based composition</i> <i>Epoxy – SBR rubber (10 phr)</i>	<i>EBNA I</i>	<i>EBNA II</i>	<i>EBNA III</i>
Reinforcements (wt%)	5 Al ₂ O ₃ fiber 5 Boron nitride 1 Silicium carbide	5 Al ₂ O ₃ fiber 10 Boron nitride 1 Silicium carbide	10 Al ₂ O ₃ fiber 5 Boron nitride 1 Silicium carbide

In the scratch test the contact between the sliding diamond indenter and the surface of the composite material is analyzed. The normal and tangential forces on indenter are recorded and the tangential stress on the surface and the interfacial stresses can be obtained.

In the frame of this present work wear resistance is evaluated only under dry conditions and 50,000 and 100,000 number of cycles of wear for the composites presented here.

In the frame of the current research, the resistance to scratch deformation is evaluated in terms of scratch depth, surface and worn volume subsequent to scratching.

Results and Discussions

Microstructure of the Composites

In [Fig. 2](#) two different specimens are shown in different diameters for different characterizations. They are manufactured by means of hot compaction technics.

General microstructures of one of the compositions are shown in [Fig. 3](#). All of the compositions showed a considerably homogenous distribution of the reinforcements in the microstructure. Essentially, it is seen that the adhesion of the rubber to the epoxy matrix is very successfully carried out after the chemical treatment. In addition, white circular particles show the alumina fibers in different sizes. Some small local agglomerations of rubbers are observed in the microstructure due to the incomplete mixture process. Because, homogenous distributions of the reinforcements need more mixture process.

After microstructure observations, Shore D hardness results are given in [Table 2](#).

From [Table 2](#) it is seen that BN particles are increasing the surface hardness better than alumina fibers.

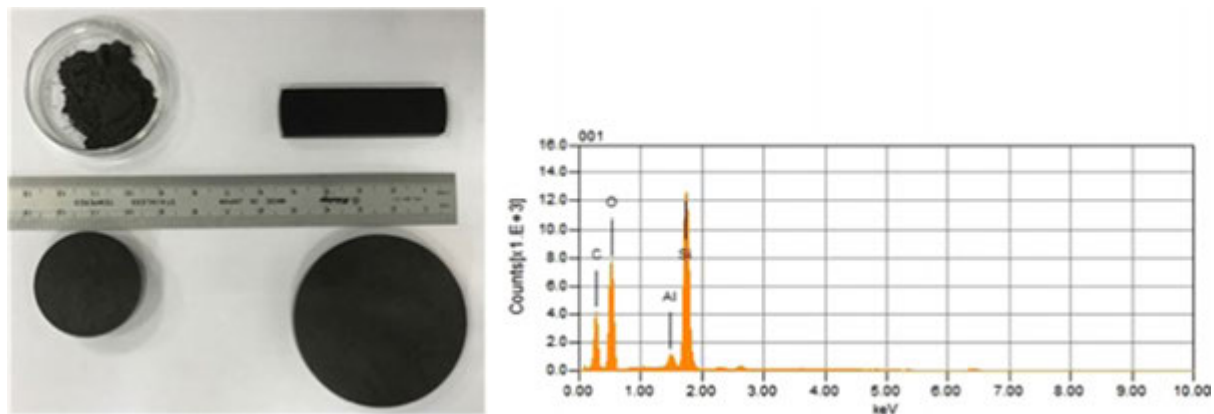


Fig. 2 Macrograph of the specimens with a diameter of $d = 30$ and 50 mm after compacting and post curing produced from recycled rubber modified epoxy based composites reinforced with (BN + Al_2O_3 + SiC + epoxy-rubber).

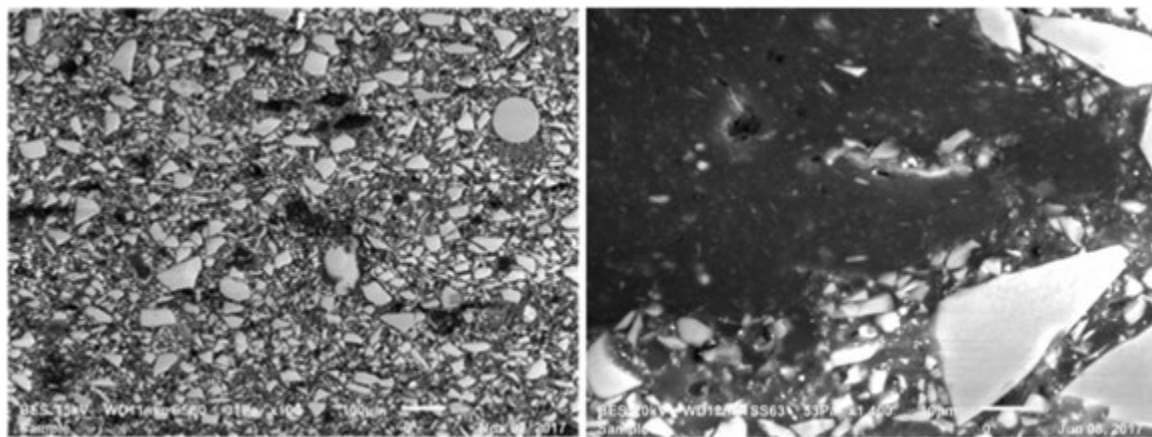


Fig. 3 Microstructure of a specimen EBNA II in low (left) and high magnification (right) showing interface of rubber with epoxy.

Thermal Analysis and Physical Characterization

After all blending and material preparation processes, DSC analyses are realized on unpolymerized powder compositions and the results are given in **Fig. 4**. From thermo-gram of DSC, it is seen that curing started slightly above the room temperature and it finished around 180°C . Also, in the same thermo-gram it can be indicated that physical and/or chemical reactions occur intensely around 240°C and they are thought as possible oxidations over 200°C [19].

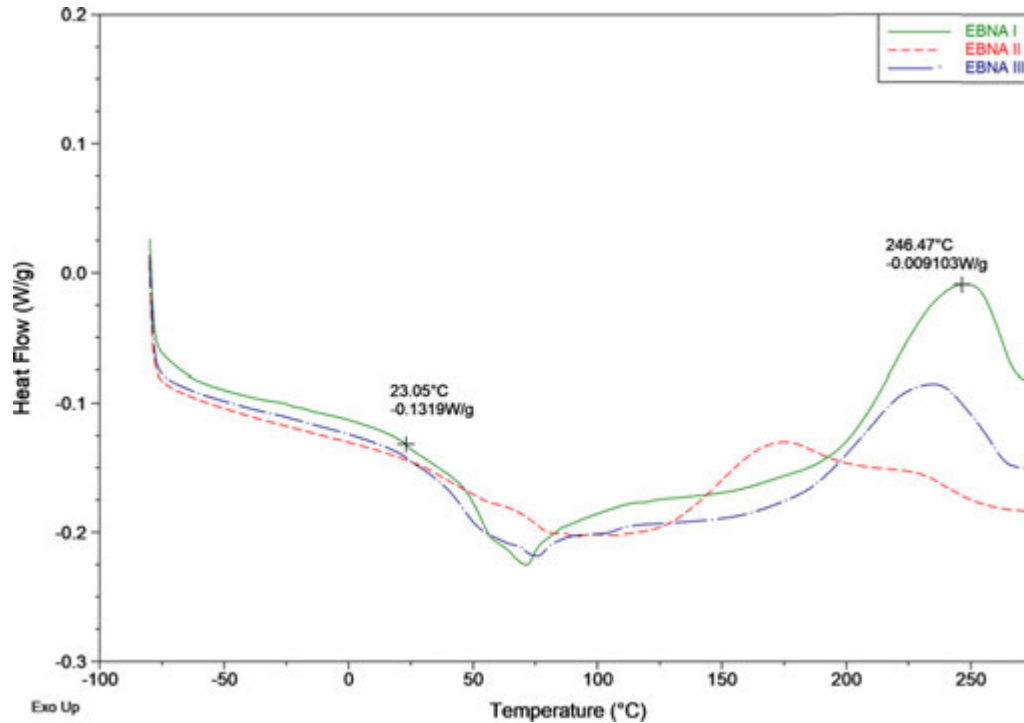
After DSC analyses, fundamental idea on elastic response and viscous response of the material are obtained respectively from storage modulus (E') and loss modulus (E'') under dynamic loading. Then, the loss factor ($\tan \delta$) is determined by taking the proportion of loss modulus to storage modulus which is a measure of the energy lost from the material under loading at different temperatures. It shows the internal friction or mechanical damping in a viscoelastic material [20]. After acquiring the results, T_g can be determined by taking the first inflection point, or the onset of the drop-in storage modulus. However, the simplest approach to determine T_g is taking the peak of $\tan \delta$ [21].

DMA analysis is important for the manufactured composites. Because, the determined glass transition temperature can be thought as a temperature limit for the structural applications. Because, mechanical resistance of these composites drops drastically after T_g and this should be considered during design process.

Fig. 5 exhibits the $\tan \delta$ and storage modulus at different temperatures for different compositions. T_g of these composites are determined between 117 – 128°C and it is seen that ascending boron nitride rate increases the T_g of these composites. From this situation it can be said that boron nitride particles lower the polymer chain mobility. Hence, BN content dominant composites remain in the elastic region for a longer wider temperature range than other compositions [22]. However, increasing amount of alumina fibers (EBNA III) promotes more energy dissipation from the material compared to (EBNA II) and it dominates the increase in the storage modulus. In addition, lower E' values under T_g gives an indication about more flexible structure of the EBNA I composites. Also, **Fig. 6** presents Cole-Cole plot where E'' data are plotted as a function of E' for EBNA composites. The shape of the Cole-Cole plots is stated to be designative of the homogeneity of the composite system. Semicircle curve demonstrates that polymeric system is homogeneous [23]. It can be seen that increased amount of BN particles alters the shape of Cole-Cole

Table 2 Hardness values of EBNA specimens

Hardness measurement	
Specimen	Shore D
EBNA I	88
EBNA II	93
EBNA III	89


Fig. 4 DSC analysis results of EBNA specimens: Evolution of heat flow as a function of temperature.

plot. For EBNA I and III compositions the Cole-Cole plot is warped semicircular, whereas for EBNA II it is quasi-round in shape. Warped semicircular suggests that there is heterogeneity among the matrix and the fibers. It is concluded that amount and shape of fillers influence the shape of Cole-Cole plot by affecting dynamic mechanical properties of these composites [24,25].

Three Point Bending Tests and Fracture Surface Observation

Three-Point Bending (3PB) tests have been carried out for each different type of composites.

Flexural stress is calculated during three-point bending test according to the Eq. 1:

$$\sigma = \frac{3Pl}{2bh^2} \quad (1)$$

In this formula, l is the span length, P is the maximal bending load, b and h are the sample thickness and depth, respectively. Flexural strain, ε_f , is determined according to the Eq. 2:

$$\varepsilon_f = \frac{6Dh}{l^2} \quad (2)$$

D is the maximum deflection at the center of the specimen.

E_B is the modulus of elasticity in bending and it is expressed with the Eq. 3 as follows:

$$E_B = \frac{l^3 m}{4bd^3} \quad (3)$$

m is the tangent of the initial straight portion of the stress-strain curve.

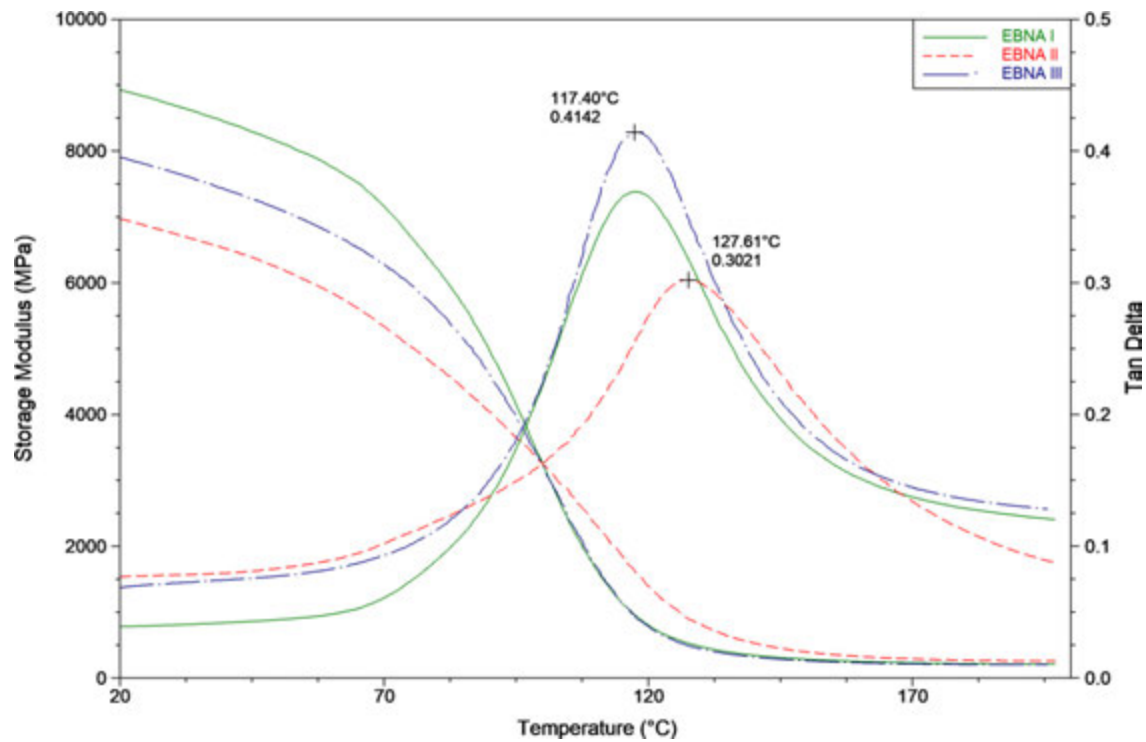


Fig. 5 Evolution of storage modulus as a function of the temperature for three EBNA specimens.

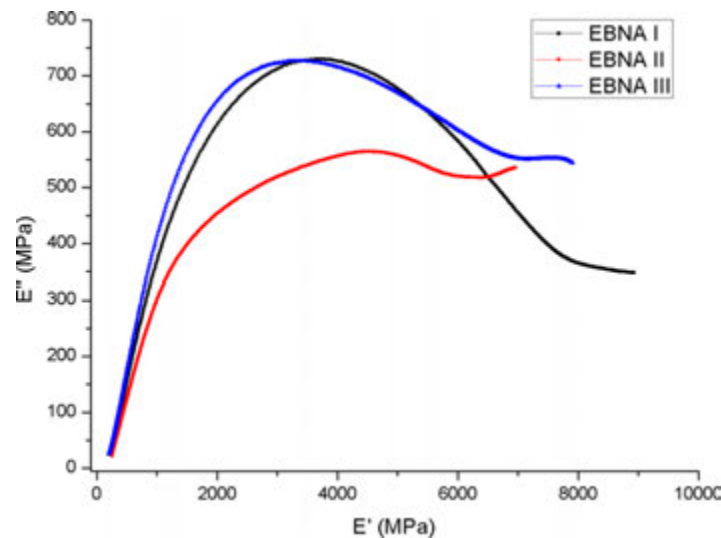


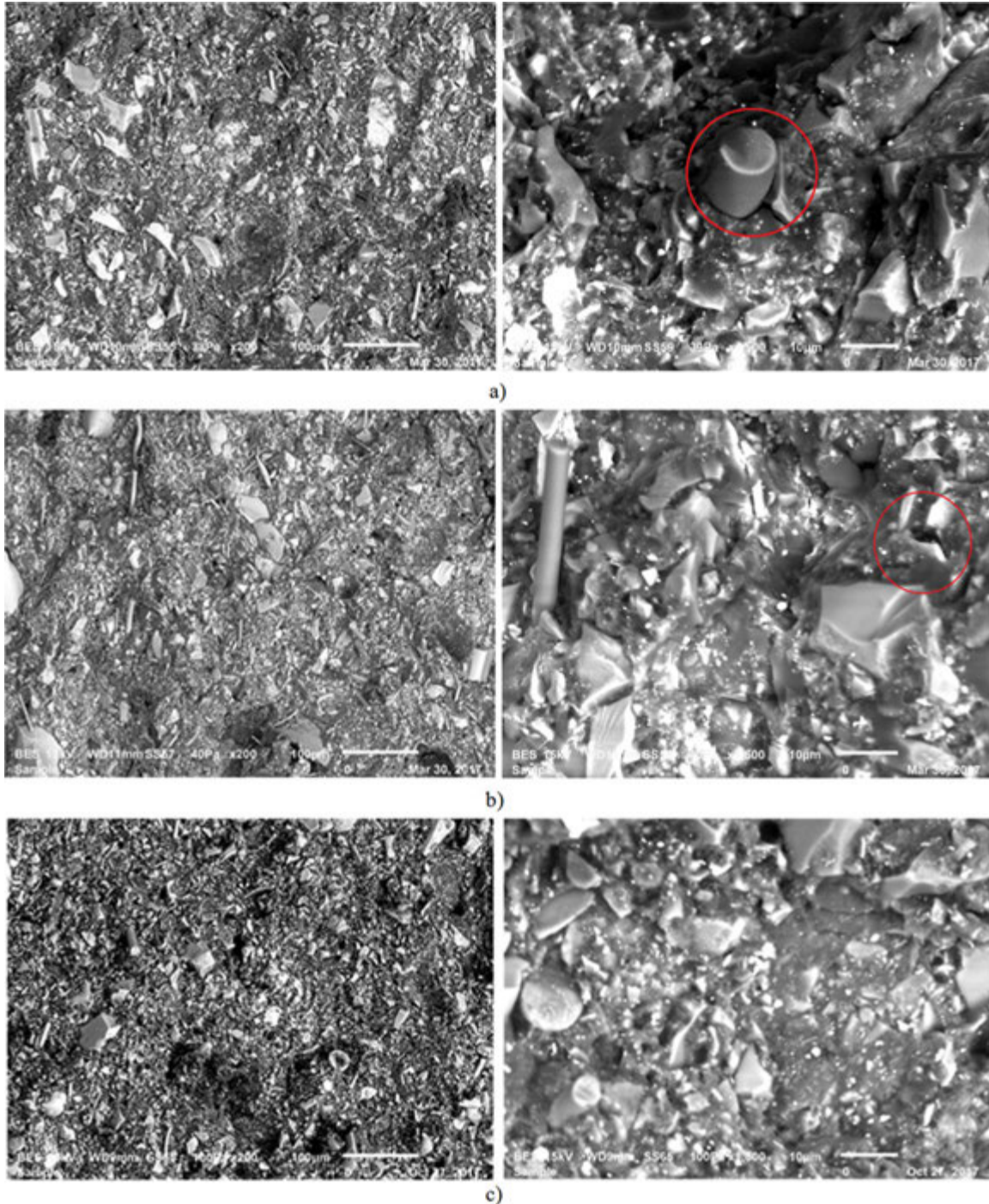
Fig. 6 Cole-Cole plot for EBNA composites.

From [Table 3](#), one can comment that alumina fibers are more efficient to increase the flexural strength and modulus compared to boron nitride. Also, excessive amount of boron nitride particles has detrimental effect on modulus values. This situation is commented as the existence of agglomerated BN particles behaves as stress concentrators. On the other hand, modulus and strength values for the matrix show considerably large standard deviations. Therefore, important fluctuations between different specimens are observed. Despite the increasing trend at strain values, matrix is seen still more flexible than the composites. However, more precise determination requires fracture toughness calculations with notched specimens.

After 3PB tests, SEM observation is done on fracture surfaces. [Fig. 7](#) shows the fracture surfaces of EBNA I-II-III composites in different magnifications. As first impression, it can be commented that rough fracture surfaces give a sign about the good adhesion between matrix and reinforcements. Also, the fibers which are perpendicular to fracture surface created a link (crack bridging in

Table 3 Comparison of mechanical properties of EBNA specimens

Composition name	Ultimate flexural stress (MPa)	Flexural modulus (GPa)	Strain at break (ϵ %)
Matrix	4213 $\pm$ 605	788 $\pm$ 079	066 $\pm$ 007
EBNA I	1150 $\pm$ 120	687 $\pm$ 018	030 $\pm$ 003
EBNA II	2288 $\pm$ 190	470 $\pm$ 016	057 $\pm$ 002
EBNA III	4251 $\pm$ 243	815 $\pm$ 016	059 $\pm$ 006


Fig. 7 Fracture surfaces in low (left) and high (right) magnification after impact testing (a) EBNA I (b) EBNA II (c) EBNA III respectively.

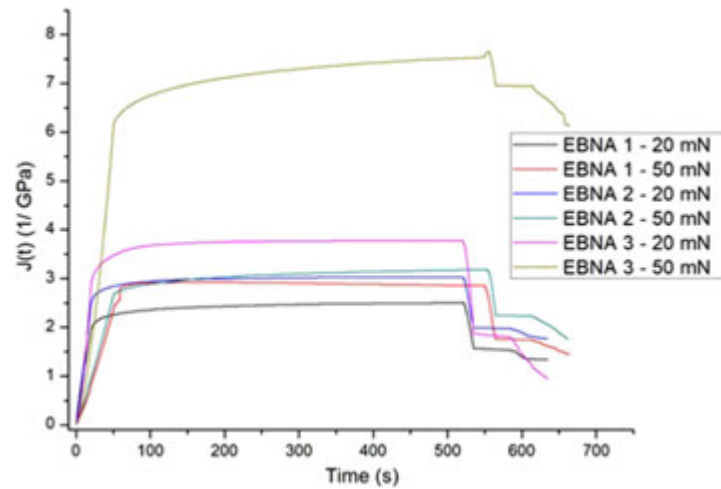


Fig. 8 Creep Compliance curves for specimens EBNA I-II-III, under 20 mN and 50 mN load.

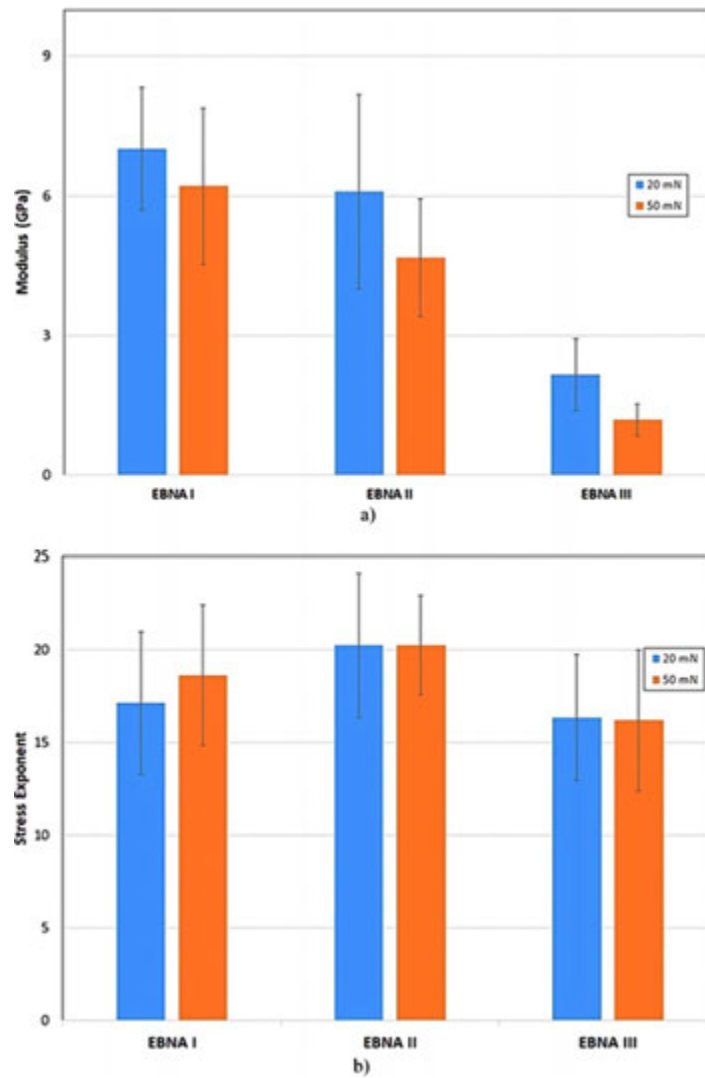


Fig. 9 (a) Indentation modulus (b) stress exponent for EBNA composites under 20 mN and 50 mN.

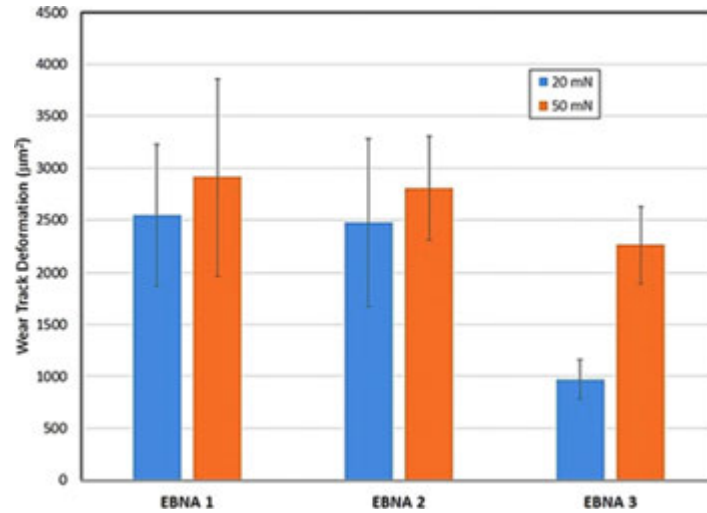


Fig. 10 Comparison of wear track deformation for EBNA composites.

Fig. 6(a) inside red circle) between two sides of the crack and it has a positive effect against to crack opening. In recycled rubber modified epoxies the main toughening mechanism is thought as crack deflection with the secondary contributions of shear deformations [26] but here important mechanism is attributed to crack blunting (in **Fig. 6(b)** inside red circle) by a hard particle as well as bridging effect of fibers.

3.4 Time Dependent Behaviour by Means of Nano-Indentation

During each test, data collected is used to calculate the creep compliance and the stress exponent defined in Eq. 4 [27]:

$$\varepsilon(t) = \sigma_0 J(t) \quad (4)$$

where σ_0 is the constant stress applied and $J(t)$ is calculated using Eq. 5:

$$J(t) = A(t) / (1 - (v)) P_0 \tan \theta \quad (5)$$

In Eq. 5 $A(t)$ is the contact area, P_0 constant applied load, θ is the effective cone angle which is 70.3° for a Berkovich indenter and the Poisson's ratio V is assumed to be 0.3. This approach takes into account how the contact area under the Berkovich tip alters while displacement into the surface changes.

The strain versus time behaviour during creep is characterized by a high strain rate $\dot{\varepsilon} = d\varepsilon/dt$ in the primary stage of creep and then in the secondary, steady state stage of creep, the strain rate is given in Eq. 6 can be written as:

$$\dot{\varepsilon} = K \sigma^n \quad (6)$$

where K is a constant and n is the stress exponent. The strain rate is calculated in the software and in turn n is obtained from the log-log plot of strain rate versus stress in the secondary stage of creep.

The materials under consideration are heterogeneous in nature and the fact that the nano-indentation test is carried out over a small area/volume, a large scatter in the data is observed and to overcome this sampling number is taken as large as possible then **Fig. 7** is plotted from the average values.

According to **Fig. 8**, creep compliance is improving with the increasing amount of alumina fibers which means that EBNA III has a higher capacity to flow in return to an applied stress [28,29]. Also, the creep compliance is obviously dependent on the indentation forces between 20 and 50 mN.

Besides, the trends in the compliance values with time seem alike for different force levels examined with Berkovich tip, and this implies dissimilarity of the time-dependent behaviour from stress-dependent behaviour [30].

Results may be compared with linear viscoelastic models. However, these models do not consider the case of tip-specimen adhesion which may differ from experimental results.

From **Fig. 9(b)** it is seen that, increasing BN amount results in an increase in the stress exponent which means that viscoelastic characteristic of the material is improved. On the other hand, by the increase in the reinforcement rate modulus is not improved as in the 3PB testing as seen in **Fig. 9(a)**. For this reason, these values should be compared with the values obtained from the other methods.

Whether or not indenter tip comes across a BN rich zone or a matrix rich area on the specimen will introduce error into this method. Hence, whilst the amount of BN increases, the error bars become larger. Different researchers have indicated for polymers and polymer-based composites that modulus as determined by nano-indentation is higher than that determined by macroscopic tensile tests. This inequality is thought as a consequence of pile up of material around the contact impression and viscoelasticity of

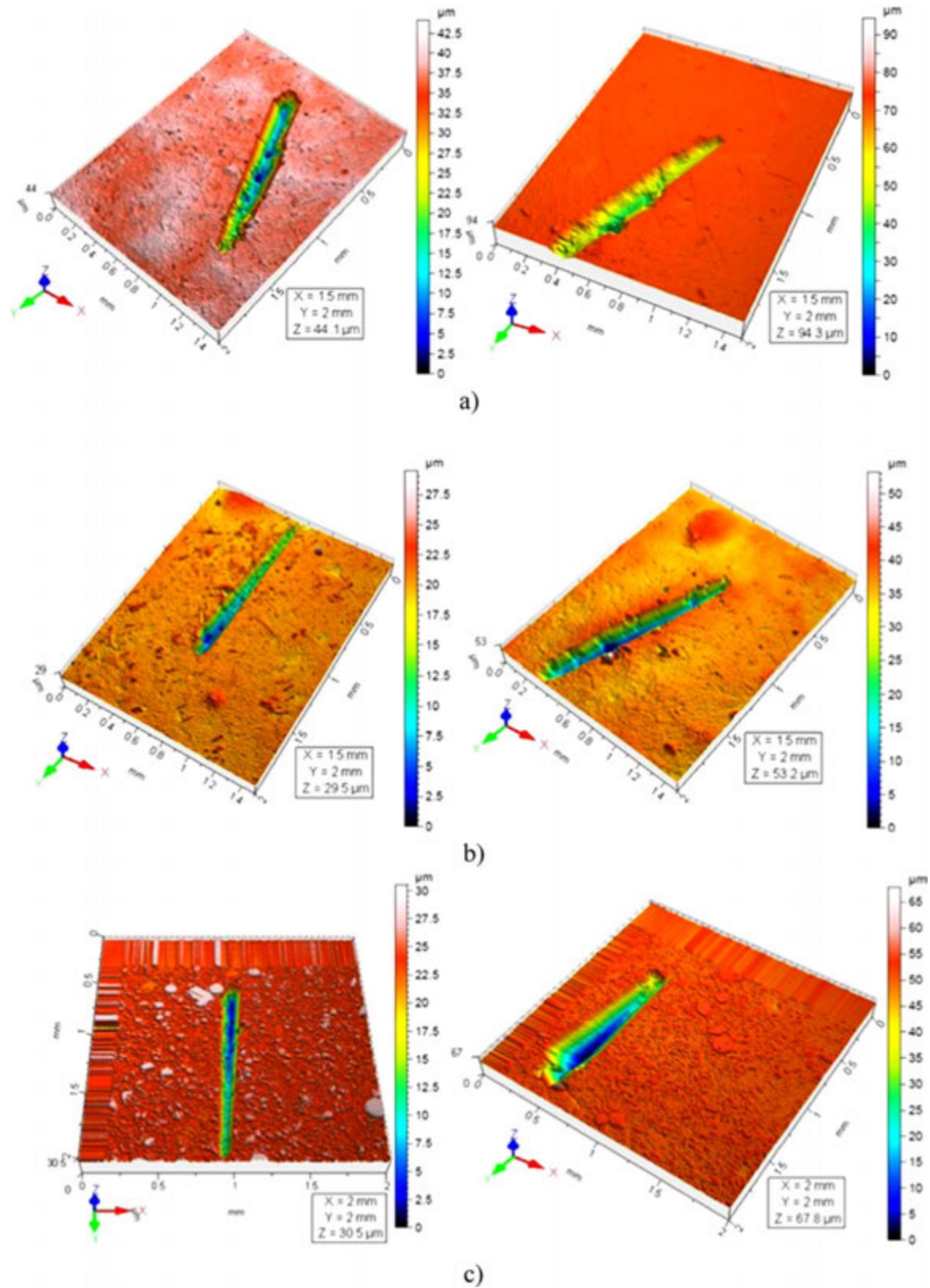


Fig. 11 Three-dimensional damage traces obtained in the direction of width and length for (a) EBNA I (b) EBNAII (c) EBNA III for 50 k cycles and for 100 k cycles.

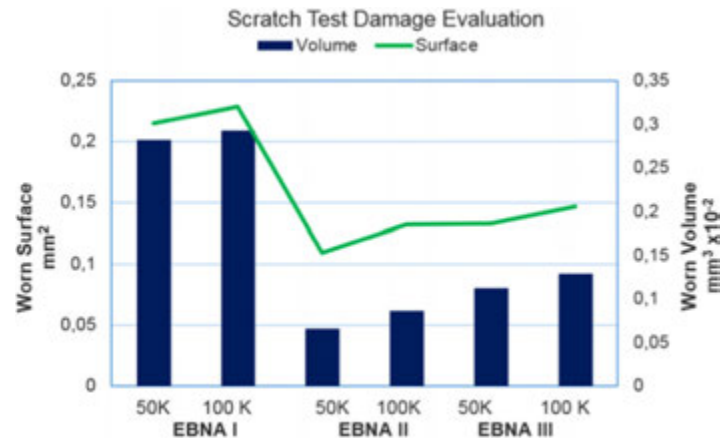


Fig. 12 Worn surface and worn volume after scratch tests.

the polymer and polymer based composites which are not taken into consideration during the modulus determination by the Olivier-Pharr method [31].

Wear Testing by Nanoindentation

Last but not least, nano-indenter is used to obtain scratches over the specimen. One cycle is defined as a pass and return of the indenter over the track, so the total distance covered for one wear test is 0.050 m. Speed of the tip during wear tests is 50 $\mu\text{m/s}$.

Total of 10 wear tests for each specimen are performed under the two normal loads. The wear in a track is characterized as the area between the initial profile and the residual profile of the wear track.

In the same way, the averages of the wear track deformation are shown in Fig. 10.

Increase in alumina fiber content result in higher surface deformation in nano scale. However, to comment properly on wear resistance, lost volume and damaged surface evaluation after tests is considered more trustworthy. For this reason, macro scratch tests are realized to see the more accurate wear resistance.

Damage Analysis by Means of Scratch Test and 3D Optical Roughness Meter

After realizing two different group of macro scratch tests, three dimensional damages are obtained by a 3D optical surface scanner. The results are presented in the Fig. 11.

In Fig. 12 the volume and surface of the damage trace after scratch calculated from roughness test results are given. Fig. 12 indicates that thanks to the hard nature of BN particles, EBNA II composites have less damage. Hard particles provide a more wear resistant material upon homogeneous distribution. In reality, because of the high shear stress at the interfaces the interfacial shear stress should probably be the main reason for damage of the matrix and reinforced filler interfaces. When the indenter is slipping, tangential tensile stress is caused on the surface behind the indenter, while in front of the indenter the tangential stress is compressive.

Conclusions

After manufacturing of epoxy-recycled rubber based composites, microstructure is observed with SEM. From the images, a homogeneous distribution of the reinforcements is observed. However, in minor scale certain agglomerations of rubbers is detected. This situation arises from limited milling duration. On the other hand, there is a risk of degradation in properties if the milling time is kept excessively long.

Second, alumina fibers are found more efficient than BN to improve the mechanical strength. However, the flexibility of material decreases by the addition of reinforcements. In addition, modulus values obtained from nano indentation, differ from the macro test results. This is considered as a consequence of pile up of material around the contact impression and viscoelasticity of the polymer. Furthermore, creep compliance values presented that alumina fibers provide a higher capacity to flow in return to an abruptly applied stress.

Another important point is that, BN particles have increased the T_g of the composites whereas alumina fibers did not influence it noticeably. This indicates that alumina fibers do not affect the polymer chain mobility as much as BN.

In addition, scratch test results showed that BN particles are efficient against to wear thanks to its hard nature. Last but not least, after mechanical tests, fracture surfaces are observed by means of SEM to identify toughening mechanisms. Crack deflection and crack blunting with the contribution of fiber bridging are thought as the main toughening mechanisms.

By considering all material characterization results, these novel composites can be used in micro electric industry as component base material thanks to their advantageous properties in mechanical and thermal aspects.

References

- [1] Zhou, W.-Y., Qi, S.-H., Zhao, H.-Z., Liu, N.-L., 2007. Thermally conductive silicone rubber reinforced with boron nitride particle. *Polymer Composites* 28 (1), 23–28.
- [2] Wattanakul, K., Manuspiya, H., Yanumet, N., 2011. Thermal conductivity and mechanical properties of BN-filled epoxy composite: Effects of filler content, mixing conditions, and BN agglomerate size. *Journal of Composite Materials* 45 (19), 1967–1980.
- [3] Mamunya, Y.P., Davydenko, V.V., Pissis, P., Lebedev, E.V., 2002. Electrical and thermal conductivity of polymers filled with metal powders. *European Polymer Journal* 38 (9), 1887–1897.
- [4] Partridge, G., 1992. Inorganic materials V. Ceramic materials possessing high thermal conductivity. *Advanced Materials* 4 (1), 51–54.
- [5] Hsieh, C.-Y., Chung, S.-L., 2006. High thermal conductivity epoxy molding compound filled with a combustion synthesized AlN powder. *Journal of Applied Polymer Science* 102 (5), 4734–4740.
- [6] Branch, M., 2011. Preparation of nano-scale α -Al₂O₃ powder by the sol-gel method. *Ceramics-Silikáty* 55 (4), 378–383.
- [7] Amirshaghghi, A., Kokabi, M., 2010. Tailoring size of α -Al₂O₃ nanopowders via polymeric gel-net method. *Iranian Polymer Journal* 19 (8), 615–624.
- [8] Zhang, Z., Lei, H., 2008. Preparation of α -alumina/polymethacrylic acid composite abrasive and its CMP performance on glass substrate. *Microelectronic Engineering* 85 (4), 714–720.
- [9] Williams, J.G., 1984. *Fracture Mechanics of Polymers*. Ellis Horwood Ltd, Publisher. (ISBN-13: 978-0853126850).
- [10] Dhingra, A.K., 1980. Metal matrix composites reinforced with fibre FP (α -Al₂O₃). *Philosophical Transactions of the Royal Society of London Series A Mathematical and Physical Sciences*. 559–564.
- [11] Adhikari, B., De, D., Maiti, S., 2000. Reclamation and recycling of waste rubber. *Progress in Polymer Science* 25, 909–948.
- [12] Fiksel, J., Bakshi, B., Baral, A., Guerra, E., DeQuervain, B., 2011. Comparative life cycle assessment of beneficial applications for scrap tires. *Clean Technologies and Environmental Policy* 13, 19–35.
- [13] Fang, Yi., Zhan, M., Wang, Y., 2001. The status of recycling of waste rubber. *Materials & Design* 22 (2), 123–128.
- [14] Mangaraj, D., 1997. *Proceedings of the International Conference on Rubbers*, p. 61. Calcutta, India.
- [15] Oliphant, K., Baker, W.E., 1993. The use of cryogenically ground rubber tires as a filler in polyolefin blends. *Polymer Engineering & Science* 33 (3), 166–174.
- [16] Naskar, A.K., Anil, K.B., De, S.K., 2001. Thermoplastic elastomeric composition based on ground rubber tire. *Polymer Engineering & Science* 41 (6), 1087–1098.
- [17] Naskar, A.K., De, S.K., Bhowmick, A.K., 2002. Thermoplastic elastomeric composition based on maleic anhydride-grafted ground rubber tire. *Journal of Applied Polymer Science* 84 (2), 370–378.
- [18] ASTM Spec. Tech. Publ, 1987. *N184 A Glossary of Terms Relating to Rubber and Rubber Technology*. American Society for Testing and Materials.
- [19] Irez, A.B., Bayraktar, E., Miskioglu, I., 2017. Design and mechanical-physical properties of epoxy-rubber based composites reinforced with nanoparticles. *Procedia Engineering* 184, 486–496.
- [20] Menard, K.P., 2008. *Dynamic Mechanical Analysis: A Practical Introduction*. CRC press.
- [21] Li, G., Lee-Sullivan, P., Thring, R.W., 2000. Determination of activation energy for glass transition of an epoxy adhesive using dynamic mechanical analysis. *Journal of Thermal Analysis and Calorimetry* 60 (2), 377–390.
- [22] Thomas, R., Yumei, D., Yuelong, H., *et al.*, 2008. Miscibility, morphology, thermal, and mechanical properties of a DGEBA based epoxy resin toughened with a liquid rubber. *Polymer* 49 (1), 278–294.
- [23] Uma Devi, L., Bhagawan, S.S., Thomas, S., 2010. Dynamic mechanical analysis of pineapple leaf/glass hybrid fiber reinforced polyester composites. *Polymer Composites* 31 (6), 956–965.
- [24] Ferry, J.D., 1980. *Viscoelastic Properties of Polymers*. New York: John Wiley and Sons, Inc.
- [25] Jawaid, M., *et al.*, 2013. Effect of jute fibre loading on tensile and dynamic mechanical properties of oil palm epoxy composites. *Composites Part B Engineering* 45 (1), 619–624.
- [26] Kaynak, C., Sipahi-Sagliam, E., Akovali, G., 2001. A fractographic study on toughening of epoxy resin using ground tyre rubber. *Polymer* 42 (9), 4393–4399.
- [27] Irez, A.B., Bayraktar, E., Miskioglu, I., 2018. Mechanical characterization of epoxy–scrap rubber based composites reinforced with alumina fibers. In: Thakre, P.R., Singh, R., Slipher, G. (Eds.), *Mechanics of Composite and Multi-functional Materials*, vol. 6. Cham: Springer, pp. 59–70.
- [28] VanLandingham, M.R., Chang, N.-K., Drzal, P.L., White, C.C., Chang, S.-H., 2005. Viscoelastic characterization of polymers using instrumented indentation. I. Quasi-static testing. *Journal of Polymer Science Part B Polymer Physics* 43 (14), 1794–1811.
- [29] Ting, T.C., 1966. The Contact Stresses Between a Rigid Indenter and a Viscoelastic Half-Space. *ASME*.
- [30] Lagoudas, D.C., Thakre, P.R., Benzerga, A.A., 2006. Nanoindentation of cnt reinforced epoxy nanocomposites. In: Gdoutos, E.E. (Ed.), *Fracture of Nano and Engineering Materials and Structures*. Springer, pp. 649–650.
- [31] Tranchida, D., Piccarolo, S., Loos, J., Alexeev, A., 2006. Accurately evaluating Young's modulus of polymers through nanoindentations: A phenomenological correction factor to the Oliver and Pharr procedure. *Applied Physics Letters* 89 (17), 171905.

Development of Low-Cost Graphene-Polymer Blended In-House Filament for Fused Deposition Modeling

Rupinder Singh and Ranvijay Kumar, Guru Nanak Dev Engineering College, Ludhiana, India

© 2017 Elsevier Inc. All rights reserved.

This is a reproduction of Rupinder Singh, Ranvijay Kumar, Development of Low-Cost Graphene-Polymer Blended In-House Filament for Fused Deposition Modeling, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2017, doi:[10.1016/B978-0-12-803581-8.10335-2](https://doi.org/10.1016/B978-0-12-803581-8.10335-2).

Introduction

Graphene (Gr) is a two-dimensional material having remarkable properties like high Young's modulus, ability to be thermally and electrically superconductive (high mobility of charge and electron), surface insulating behavior, and large aspect ratio for prototype fabrication. Graphite is a low-cost raw source for extraction of Gr. The Gr is generally extracted via different methods of processing, such as chemical vapor deposition (CVD), micromechanical exfoliation, ball milling, etc. (Park and Ruoff, 2009; Su *et al.*, 2011; Calderon-Ayala *et al.*, 2017). The previous studies reveal that the exfoliation process can also be used for chemical processing of graphite in water for Gr production using 1-pyrenesulfonic acid sodium salt (Yang *et al.*, 2013). Graphite is the best and most economical source for the extraction of Gr material. The literature review highlights that the oxidative treatment of graphite resulted in formation of graphite oxide (GO) for extraction of Gr (Hummers and Offeman, 1958; Mao *et al.*, 2012). The oxidation and exfoliation mechanisms for GO production were explained by Shao *et al.* (2012), Lopez *et al.* (2016), and Monajemi (2017). Synthesis of Gr through exfoliation of natural graphite in ortho-dichloro benzene (ODCB) has been achieved by a process called "sonication," (Sahoo *et al.*, 2013). All Gr extraction techniques contributed to achieve specific mechanical, optical, and thermal properties, as CVD led to Gr sheet production with high mechanical strength (Choi *et al.*, 2010; Zhao *et al.*, 2016). A highly sensitive behavior of Gr in terms of thermal and electrical conductivity made it eligible for its applications in fabrication of biosensing devices, electronic circuit charge storage devices, and medical biosensors (Irudayaraja, 2012; Obeng and Srinivasan, 2011; Hantel, 2013). This excellent material behavior of Gr extracted from graphite has been best applicable to the three-dimensional (3D) printing (fused deposition modeling, FDM) of components for high quality sensors, medical devices, and precision mechanical and electrical tools. FDM has emerged as a revolution in the field of additive manufacturing (AM) where one can fabricate complex 3D structures. FDM setup requires a .STL file format of 3D geometrical shape prepared on software. These geometrical .STL files are further mathematically oriented and sliced for prototype fabrication (Liou, 2008; Kumar *et al.*, 2012). Fig. 1 shows two spools of feedstock filament (i.e., support and build material) fed through a heating arrangement to provide molten deposition through the heater nozzle. The heater nozzle moves in the direction as geometrical shapes are oriented and sliced through G-code and M-code.

Most of the studies related to the FDM process applications highlighted the preprocessing and postprocessing of prototypes (Nunez *et al.*, 2015; Equbal and Sood, 2015; Goyanes *et al.*, 2015; Singh and Singh, 2015; Srivastva *et al.*, 2015). FDM has emerged as a specific tool for analysis by fabricating functional prototypes (Guerrero-Villar *et al.*, 2015). It has been reported that FDM technology covers almost every area of application. For example, in the medical field, a device oral pulsatile for release of drugs and patient-tailored tablet has been fabricated by FDM (Skowrya *et al.*, 2014; Melocchi *et al.*, 2015). In this article, a systematic procedure for extraction of low-cost Gr followed by development of feedstock filaments for FDM has been outlined as a case study. The thermal and electrical conductivity analysis of Gr-blended acrylonitrile butadiene styrene (ABS) polymer matrix has been performed on in-house developed feedstock filament for fabrication of functional/nonfunctional prototypes.

Materials and Method

Materials

Low-cost Gr-blended feedstock filament can be prepared through use of graphite powder. Commercial ABS polymer and graphite micropowder was procured from the local market. Graphite micropowder was processed by sieve shaker to know grain size for the purpose of Gr extraction. The ABS granules were pretreated in an oven at 70–80°C temperature for moisture removal.

ABS is an amorphous polymer that is made by polymerization of acrylonitrile and styrene in presence of catalyst polybutadiene. Acrylonitrile, which contributed 15–35%, improves cross-linking butadiene and styrene; butadiene, which contributed 5–30%, polarizes and forms long carbon chains; and styrene, which contributed 40–60%, has opaque and smooth surface properties. ABS polymer has thermal conductivity 0.1 W/m K, glass transition temperature approximately at 105°C, and no true melting point because of its amorphous nature (Matbase, 2014; ABS Prospector, 2016). Graphite is semimetallic characterized allotropes of carbon, which is available in crystalline form and is considered to be the most stable form of carbon. Graphite is an economical source for extraction of Gr powder by various physical and chemical methods. Metamorphism with the reduction of sedimentary carbon helps for the occurrence of graphite in the rock form. Quartz, calcite, and micas are some of the minerals that

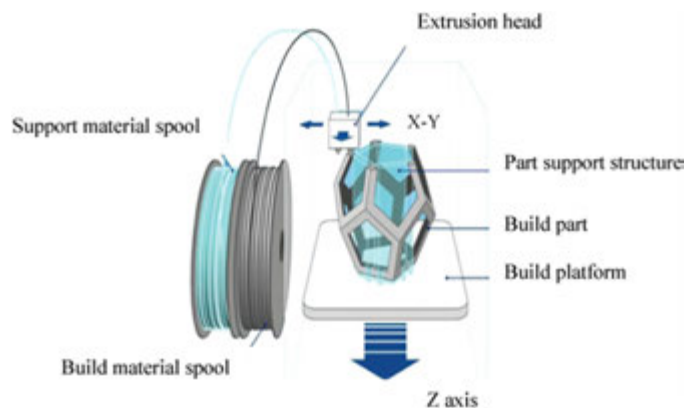


Fig. 1 Schematic of fused deposition modeling (FDM) technique. Reproduced from Kun, K., 2016. Reconstruction and development of a 3D printer using FDM technology. *Procedia Engineering* 149 (1), 203–211.

are naturally associated with graphite as foreign particle. According to surveys conducted by United States agencies, China, and India are the major producers of graphite. Graphite has the excellent properties of high thermal stability, remarkable electrical and thermal conductivity due to charge and electron mobility, good machining characteristics, and toughness.

ABS polymer matrix filled with graphite generally reduces wear as the coefficient of friction becomes smaller. Graphite as reinforcement to ABS polymer matrix led to reduction of mechanical strength and weight (see Fig. 2).

The mechanical properties of ABS polymer matrix filled with graphite are less than the parent material. But Gr extracted from graphite improves the ABS polymer matrix and their mechanical properties are much greater than the parent ABS plastic. The addition of carbon nanotube (CNT) and Gr in ABS matrix as a filler improves the thermal and electrical conductivities (Wang *et al.*, 2015). Figs. 3(a) and (b) show that electrical conductivity of ABS matrix was increased as CNT contents increases and at 0.06% CNT level the *V-I* characteristics were obtained as desired.

Various studies have been conducted to investigate the effect of Gr content incorporated into the polymer matrix. In a study conducted by Dul *et al.* (2016), an effect of heat flow rate has been observed for compression molded (CM), extruded (E), and 3D printed (H) natural ABS and ABS-4% Gr composites. Fig. 4 shows that 3D printed parts with 4% Gr contents achieved maximum heat flow.

Method and Procedure

Extraction of Gr for development of feedstock filament for FDM

Exfoliation is a chemical approach for removal of GO from graphite dissolution to achieve Gr extraction (Sahoo *et al.*, 2013). The exfoliation process forms chemically converted stable Gr from graphite powder with much lower production cost (Eda *et al.*, 2008; Xu *et al.*, 2008; Li *et al.*, 2008). Fig. 5 shows the process of exfoliation through which feedstock filaments are developed for 3D printing. In this case study a 3D printed part has been used as a specimen for thermal analysis by standard Lee's disk method.

Some common organic chemicals (e.g., benzene, toluene, nitrobenzene) have been reported for use as catalyst for chemical exfoliation of graphite. Further *N*-dimethyl-formamide (DMF) and *N*-methylpyrrolidone (NMP) have been used to form homogeneous dispersion of Gr (Niyogi *et al.*, 2003; Blake *et al.*, 2008; Hernandez *et al.*, 2008; Hamilton *et al.*, 2009). Except chemical exfoliation some studies have been reported for exfoliation through electrochemical, water dispersion and other mode of dispersion (Su *et al.*, 2011; Yang *et al.*, 2013; Zhou *et al.*, 2014; He *et al.*, 2015; Sharma *et al.*, 2015). The detailed procedure has been shown in Fig. 5. The mixing of graphite in organic solvent contributed to the mixing of graphite dissolution. Further the treatment in ultrasonic bath followed by centrifugation provides separation of graphite flakes from Gr. The aging of Gr dissolution contributed to the stabilization of Gr layers in solution. After this the graphite flakes are removed to extract the Gr through pipetting. The Gr is further mechanically blended with ABS granules for the preparation of feedstock filament by twin screw extrusion process. Finally the prepared feedstock filaments were fed to the commercial FDM setup for preparation of 3D parts (in disk shape) to be used for thermal and electrical analysis.

Experimentation

Initially the pilot experimentation was conducted for extraction of Gr through exfoliation of graphite flakes with naphthalene powder in NMP solution under experimental conditions suggested in Fig. 5. The unexfoliated layer was considered as extracted Gr from graphite dissolution. Extracted Gr was then mechanically mixed with ABS granules to blend and extrude through the twin screw extruder. The feedstock filament has been prepared by twin screw extruder under maintained input process variables, and was fed into commercial FDM (3D printer) to fabricate a disk shape pattern for thermal and electrical analysis.

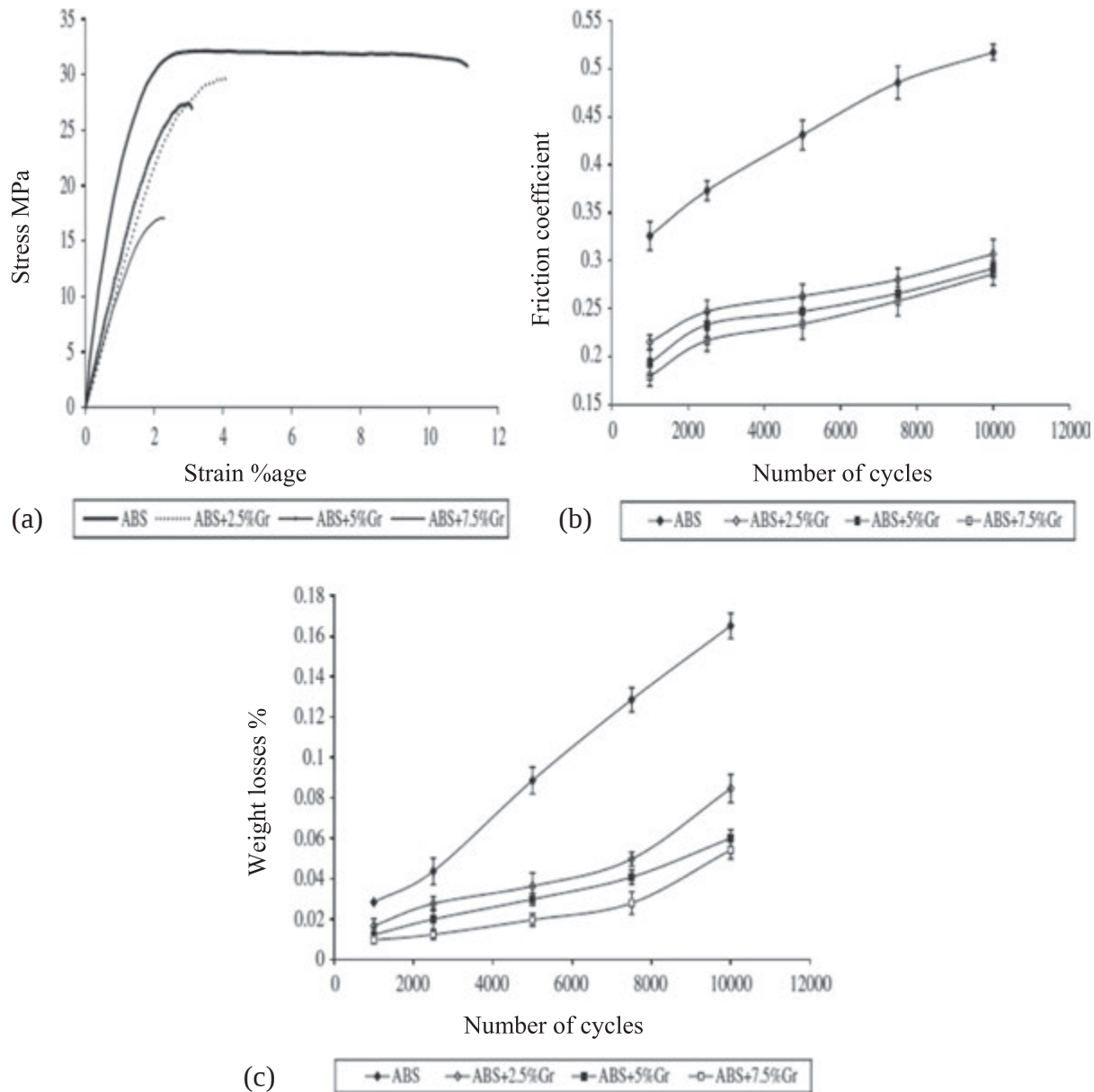


Fig. 2 Effect of graphite content on (a) mechanical strength, (b) coefficient of friction, and (c) weight loss. Reproduced from Difallah, B.B., Kharat, M., Dammak, M., Monteil, G., 2012. Mechanical and tribological response of ABS polymer matrix filled with graphite powder. *Materials & Design* 34 (1), 782–787.

Gr Extraction

Chemical exfoliation of graphite powder has been performed with chemical mixing of graphite with naphthalene powder in NMP solution followed by holding in ultrasonic bath for 90 min at 50°C and centrifugation for 60 min at 2000 rpm at room temperature. Continuous aging for 24 h has contributed to the separation of Gr layer from graphite flakes. Pipetting was performed to collect the Gr layer as to separate the graphite flakes. [Fig. 6](#) shows the Gr extraction by exfoliation process.

Twin Screw Extrusion

After mechanical mixing of ABS granules with extracted Gr from chemical exfoliation process, extrusion has been performed to achieve feedstock filaments. Thermo Scientific HaaKE MiniCTW microconical twin screw compounder has been used for feedstock filament preparations. [Fig. 7](#) shows a schematic of the twin screw extruder setup.

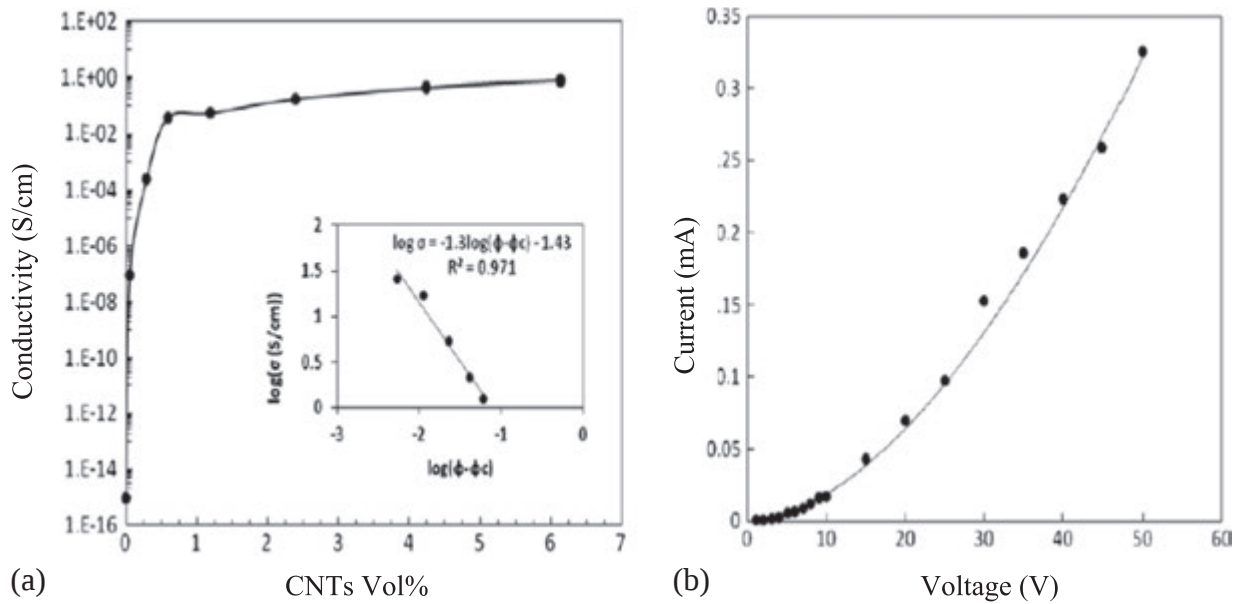


Fig. 3 (a) Thermal conductivity with varying carbon nanotube (CNT) proportions. (b) Current-voltage relationship for 0.06 vol% CNT/ABS nanocomposite. ABS, acrylonitrile butadiene styrene. Reproduced from Al-Saleh, M.H., Al-Hamid, H.K., Hussain, Y.A., 2013. CNT/ABS nanocomposites by solution processing: Proper dispersion and selective localization for low percolation threshold. Composite: Part A 46 (1) 53–59.

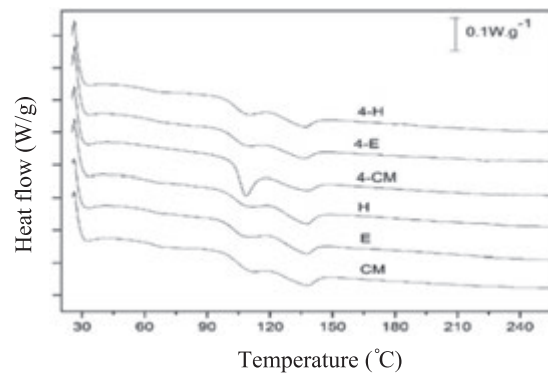


Fig. 4 Effect of Gr contents on compression molded (CM), extruded (E), and 3D printed (H) parts of acrylonitrile butadiene styrene (ABS). Reproduced from Dul, S., Fambri, L., Pegoretti, A., 2016. Fused deposition modeling with ABS-graphene nano composites. Composites: Part A. Available at: <https://dx.doi.org/10.1016/j.compositesa.2016.03.013>.

The pilot experimentations have been performed for different level of screw speed, screw temperature, and applied load conditions. On the basis of uniformity and dimensional accuracy achieved, the input process parameter has been selected as shown in Table 1.

Based upon input parametric conditions as per Table 1, a fixed proportion/composition of ABS-Gr has been fixed as 75:25 (by weight). Fig. 8 shows the extruded filament of ABS-25Gr.

FDM (3D Printing)

An .STL file extracted from designing software has been fed through the FDM setup for disk fabrication. The .STL file is sliced through Repetier-Host V0.95F software at the desired geometrical orientation and angle. The FDM setup consisted of two nozzles, one for deposition of base material and another for built part. Both nozzles are assisted with heating arrangement to melt the polymer feedstock filament.

The prepared feedstock filament was passed through the heating chamber at the desired processing conditions as shown in Table 2 to fabricate the disk part.

Fig. 9 shows Gr-blended polymer based disk prepared through FDM process illustrated in this work.

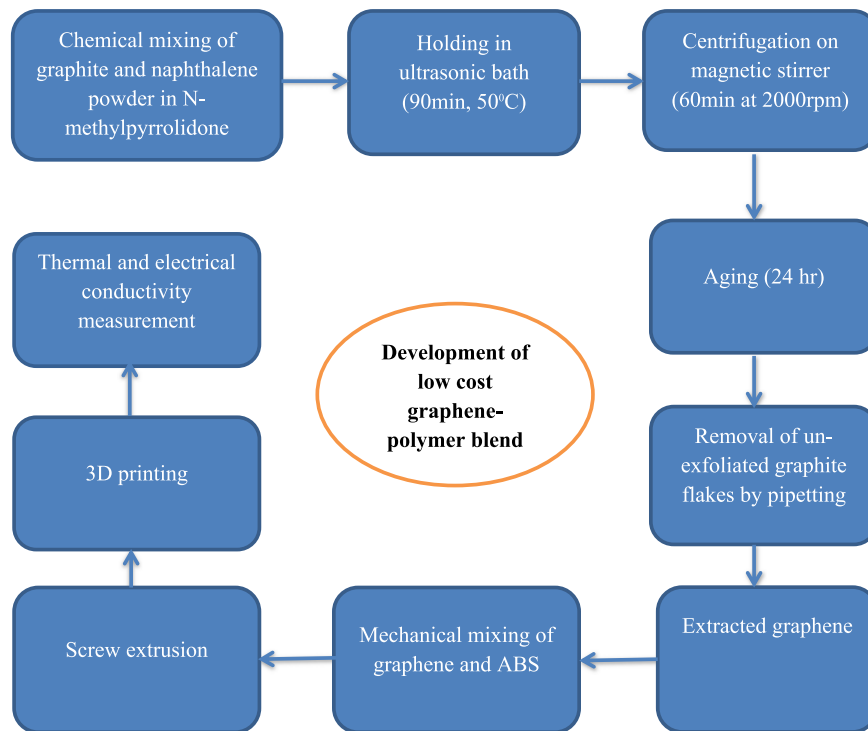


Fig. 5 Procedure for development of low-cost Gr-polymer blended in-house filament for fused deposition modeling (FDM). ABS, acrylonitrile butadiene styrene.

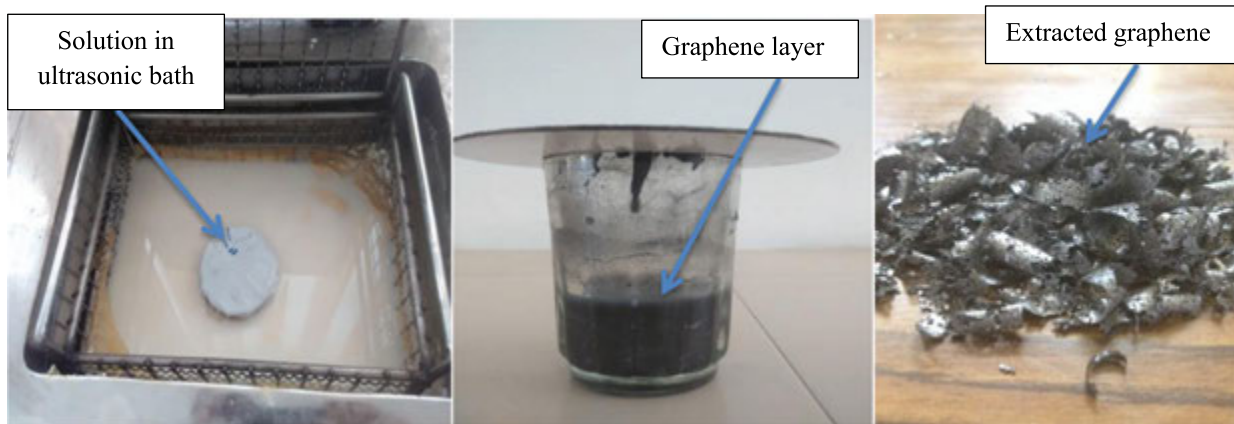


Fig. 6 Gr extraction by chemical exfoliation.

Discussion

Followed by experimentation, fabricated 3D part of disk pattern was then tested to check the effect of Gr on thermal and electrical conductivities.

Thermal Analysis (Lee's Disk Theory for Thermal Conductivity Calculation)

The disk of ABS-25Gr was fabricated on the FDM setup. Thermal analysis of the prepared disk was performed with Lee's disk method. This method for thermal analysis requires thickness and radius measurement of sample, heating arrangement for water

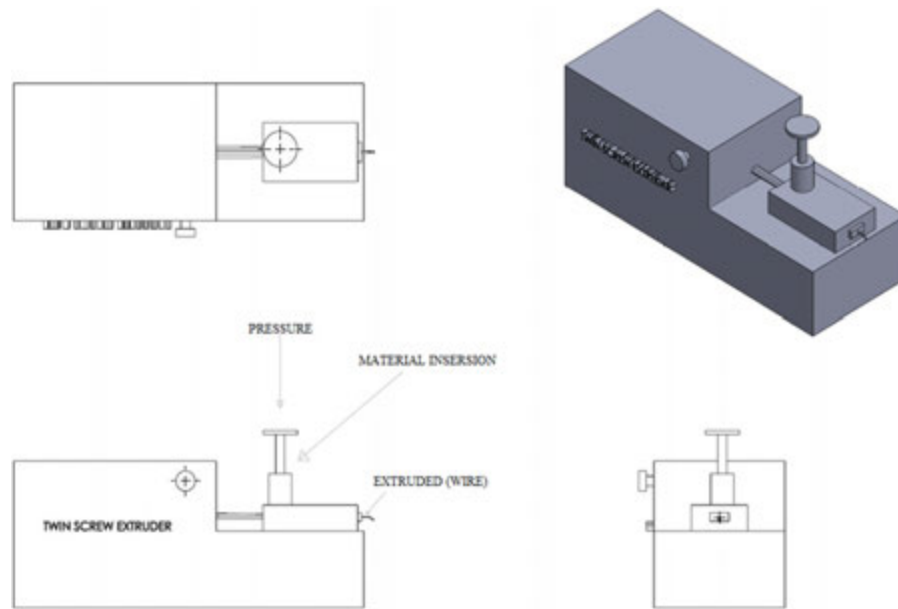


Fig. 7 Schematic of twin screw extruder.

Table 1 Process variables and their level for extrusion

<i>Input process variable</i>	<i>Operating condition</i>
Screw speed	100 RPM
Screw temperature	250°C
Applied load	10 kg

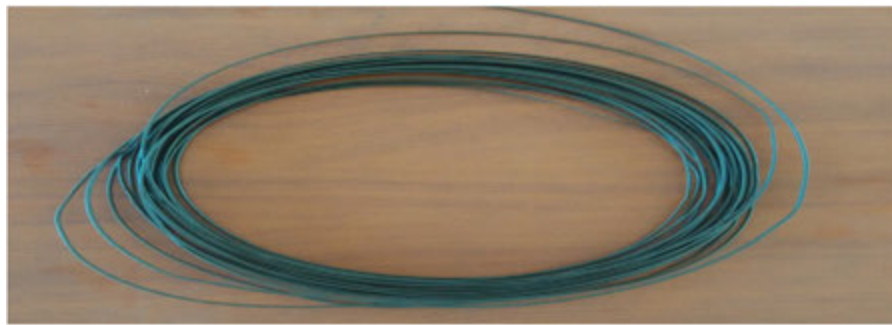


Fig. 8 Extruded feedstock filament of acrylonitrile butadiene styrene (ABS)-25Gr.

heating, and a set thermocouple for measurement of temperature differences. **Fig. 10** shows the experimental setup for thermal analysis.

As the experiment is conducted for thermal analysis, the following input has been measured:

$$\text{Steady temperature of steam chamber } (t_1) = 367\text{K} \quad (1)$$

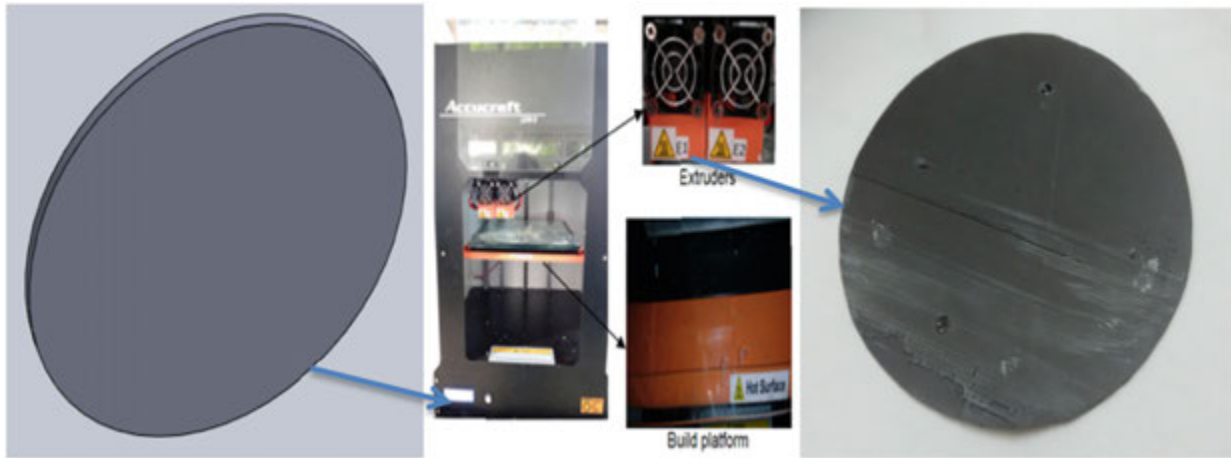
$$\text{Steady temperature of Lee's disc } (t_2) = 337\text{K} \quad (2)$$

$$\text{Mass of metallic disc } (M) = 0.769 \text{ kg} \quad (3)$$

$$\text{Specific heat capacity of Lee's disc } (S) = 377 \text{ J/kg K} \quad (4)$$

Table 2 Fused deposition modeling (FDM) process parameter and level for part fabrication

Process variable	Operating condition
Nozzle diameter	0.3 mm
Filament diameter	1.75 mm
Layer height	0.4 mm
Perimeter	3
Solid layers	Top-3; bottom-3
Fill density	0.8
Fill pattern	Honeycomb
Perimeter speed	30 mm/s
Infill speed	60 mm/s
Travel speed	130 mm/s
Extruder temperature	250°C
Bed temperature	55°C

**Fig. 9** View of commercial fused deposition modeling (FDM) setup and fabricated disk.

$$\text{Thickness of 3D printed disc sample } (x) = 0.0074 \text{ m} \quad (5)$$

$$\text{Area of sample } (A) = 0.034 \text{ m}^2 \quad (6)$$

$$\text{Temperature gradient } (dt/dT) = 3.663 \text{ K/s} \quad (7)$$

$$\text{Thermal conductivity of sample} = \frac{MS \left(\frac{dt}{dT} \right) x}{A(t_1 - t_2)} \quad (8)$$

Putting values of Eqs. (1–7) in Eq. (8)

$$= \frac{0.769 \times 377 \times 3.633 \times 0.0074}{0.034 \times 30}$$

Thermal conductivity (K) = 7.6 W/m K

Electrical Conductance Measurement

Electrical conductance (G) was calculated by evaluating potential difference (V) and current transferred (A). The resistance was measured using Ohm's law.

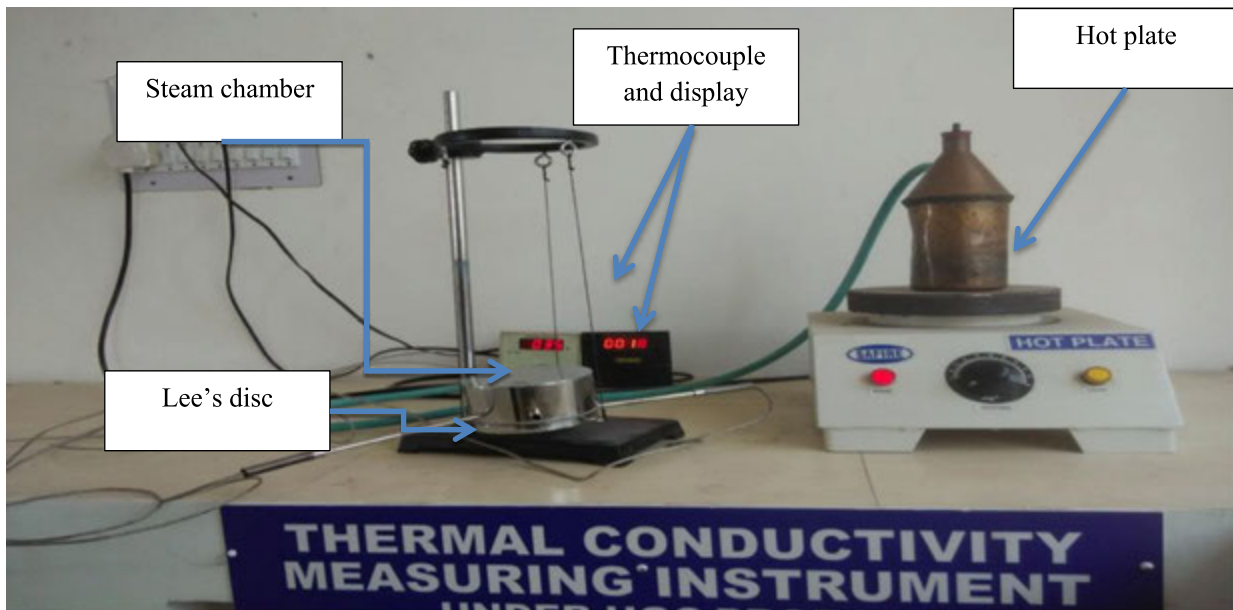


Fig. 10 Thermal conductivity measurement by Lee's disk method.

According to Ohm's law,

$$R = \frac{V}{I} \quad (9)$$

As potential difference measured, $V=2.2$ V and current, $I=5.3$ A.

Putting the values of V and I in Eq. (9), electrical resistance was calculated as,

$$R = 0.415 \, \Omega \quad (10)$$

Following the relationship between electrical conductance (G) and electrical resistance (R), the value of electrical conductance was calculated as,

$$G = 1/R \quad (11)$$

Putting the value of R in Eq. (11), it was obtained, the electrical conductance $G=2.41$ S (Seimens)

Concluding Remarks

An experimental study has been conducted for development of low-cost Gr-blended feedstock filaments of FDM followed by thermal and electrical analysis. The following observations have been made:

At lab level during graphene extraction, it was noted that from 1 kg of graphite powder approximately 20 g of graphene has been extracted. Hence it can be summarized that the chemical exfoliation process is a low-cost method for graphene extraction from graphite powder. This has led to production of low-cost feedstock filament for fabrication of functional/nonfunctional prototypes on commercial FDM setup. The thermal conductivity of natural ABS plastic was 0.01 W/m K and for ABS-25Gr 7.6 W/m K. Thermal conductivity of ABS-25Gr was calculated 76 times more than natural ABS. The excellent thermal and electrical conductivity changes of polymer matrix can lead to its application in low-cost sensors.

Acknowledgments

The authors are highly grateful to Manufacturing Research Lab (MRL), Department of Production Engineering, Guru Nanak Dev Engineering College, Ludhiana (India) for providing financial assistance to carry out the research work. The authors are also grateful to Mr. Gurleen Singh (Research Scholar, MRL Lab) and Mr. Puran Singh for fabrication of 3D parts.

References

- ABS Prospector, 2016. Available at: <https://plastics.ulprospector.com/generics/1/c/t/acrylonitrile-butadiene-styrene-abs-properties-processing>.
- Blake, P., Brimicombe, P.D., Nair, R.R., *et al.*, 2008. Graphene-based liquid crystal device. *Nano Letters* 8 (6), 1704–1708.
- Calderon-Ayala, G., Cortez-Valadez, M., Mani-Gonzalez, P.G., *et al.*, 2017. Green synthesis of reduced graphene oxide using ball milling. *Carbon Letters* 21 (1), 93–97.
- Choi, W., Lahiri, I., Seelaboyina, R., Kang, Y.S., 2010. Synthesis of graphene and its applications: A review. *Critical Reviews in Solid State and Materials Sciences* 35 (1), 52–71.
- Dul, S., Fambri, L., Pegoretti, A., 2016. Fused deposition modeling with ABS-graphene nano composites. *Composites: Part A*. Available at: <https://doi.org/10.1016/j.compositesa.2016.03.013>.
- Eda, G., Fanchini, G., Chhowalla, M., 2008. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotechnology* 3 (5), 270–274.
- Equbal, A., Sood, A.K., 2015. Investigations on metallization in FDM build ABS part using electroless deposition method. *Journal of Manufacturing Processes* 19 (1), 22–31.
- Goyanes, A., Chang, H., Sedough, D., *et al.*, 2015. Fabrication of controlled-release budesonide tablets via desktop (FDM) 3D printing. *International Journal of Pharmaceutics*. Available at: <https://doi.org/10.1016/j.ijpharm.2015.10.039>.
- Guerrero-Villar, F., Torres-Jimenez, E., Dorado-Vicente, R., Jimenez-Gonzalez, J.I., 2015. Development of vertical wind turbines via FDM prototypes. *Procedia Engineering* 132 (1), 78–85.
- Hamilton, C.E., Lomeda, J.R., Sun, Z., Tour, J.M., Barron, A.R., 2009. High-yield organic dispersions of unfunctionalized graphene. *Nano Letters* 9 (10), 3460–3462.
- Hantel, M.M., 2013. Graphite oxide and graphene oxide based electrode materials for electrochemical double layer capacitors. Doctoral dissertation, ETH Zurich.
- He, P., Zhou, C., Tian, S., *et al.*, 2015. Urea-assisted aqueous exfoliation of graphite for obtaining high-quality graphene. *Chemical Communications* 51 (22), 4651–4654.
- Hernandez, Y., Nicolosi, V., Lotya, M., *et al.*, 2008. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology* 3 (9), 563–568.
- Hummers Jr, W.S., Offeman, R.E., 1958. Preparation of graphitic oxide. *Journal of the American Chemical Society* 80 (6), 1339.
- Irudayaraja, J., 2012. Graphene for biosensing applications. *Biomedical Nanosensors* 4, 153.
- Kumar, P., Ahuja, I.P.S., Singh, R., 2012. Application of fusion deposition modeling for rapid investment casting – A review. *International Journal of Materials Engineering Innovation* 3 (3–4), 204–227.
- Li, D., Müller, M.B., Gilje, S., Kaner, R.B., Wallace, G.G., 2008. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotechnology* 3 (2), 101–105.
- Liou, F.W., 2008. Rapid Prototyping and Engineering Applications, a Toolbox for Prototype Development. London: CRC Press, Taylor & Francis Group, p. 2008.
- Lopez, M.D.P.L., Palomino, J.L.V., Silva, M.L.S., Izquierdo, A.R., 2016. Optimization of the synthesis procedures of graphene and graphite oxide. In: Pramoda, N. (Ed.), *Recent Advances in Graphene Research*. InTech. Available at: <https://doi.org/10.5772/63752>.
- Mao, S., Pu, H., Chen, J., 2012. Graphene oxide and its reduction: Modeling and experimental progress. *RSC Advances* 2 (7), 2643–2662.
- Matbase, 2014. Available at: <https://www.matbase.com/material-categories/natural-and-synthetic-polymers/thermoplastics/commodity-polymers/material-properties-of-acrylonitrile-butadiene-styrene-general-purpose-gp-abs.html#properties>.
- Melocchi, A., Parietti, F., Loreti, G., *et al.*, 2015. 3D printing by fused deposition modeling (FDM) of a swellable/erodible capsular device for oral pulsatile release of drugs. *Journal of Drug Delivery Science and Technology*. Available at: <https://doi.org/10.1016/j.jddst.2015.07.016>.
- Monajjemi, M., 2017. Liquid-phase exfoliation (LPE) of graphite towards graphene: An ab initio study. *Journal of Molecular Liquids* 230, 461–472.
- Niyogi, S., Hamon, M.A., Perea, D.E., *et al.*, 2003. Ultrasonic dispersions of single-walled carbon nanotubes. *The Journal of Physical Chemistry B* 107 (34), 8799–8804.
- Nunez, P.J., Rlwas, A., Garcia-Plaza, E., Beamud, E., Sanz-Lobera, A., 2015. Dimensional and surface texture characterization in fused deposition modeling (FDM) with ABS plus. *Procedia Engineering* 132 (1), 856–863.
- Obeng, Y., Srinivasan, P., 2011. Graphene: Is it the future for semiconductors? An overview of the material, devices, and applications. *The Electrochemical Society Interface* 20 (1), 47–52.
- Park, S., Ruoff, R.S., 2009. Chemical methods for the production of graphenes. *Nature Nanotechnology*. doi:10.1038/nnano.2009.58.
- Sahoo, S., Hatui, G., Bhattacharya, P., Dhibar, S., Das, C.K., 2013. One pot synthesis of graphene by exfoliation of graphite in ODCB. *Graphene* 2 (01), 42.
- Shao, G., Lu, Y., Wu, F., *et al.*, 2012. Graphene oxide: The mechanisms of oxidation and exfoliation. *Journal of Materials Science* 47 (10), 4400–4409.
- Sharma, V., Garg, A., Sood, S.C., 2015. Graphene synthesis via exfoliation of graphite by ultrasonication. *International Journal of Engineering Trends and Technology (IJETT)* 26, 38–42.
- Singh, R., Singh, S., 2015. Experimental investigations for statistically controlled solution of FDM assisted Nylon6–Al–Al₂O₃ replica based investment casting. *Materials Today: Proceeding* 2 (1), 1876–1885.
- Skowrya, J., Pietrzak, K., Alhnan, M.A., 2014. Fabrication of extended-release patient-tailored prednisolone tablets via 4 fused deposition modeling (FDM) 3D printing. *European Journal of Pharmaceutical Sciences*. Available at: <https://doi.org/10.1016/j.ejps.2014.11.009>.
- Srivastva, M., Maheshwari, S., Kundra, T.K., 2015. Virtual modeling and simulation of functionally graded material component using FDM technique. *Materials Today: Proceedings* 2 (1), 3471–3480.
- Su, C.Y., Lu, A.Y., Xu, Y., *et al.*, 2011. High-quality thin graphene films from fast electrochemical exfoliation. *ACS Nano* 5 (3), 2332–2339.
- Wang, F., Zhang, Y., Zhang, B.B., *et al.*, 2015. Enhanced electrical conductivity and mechanical properties of ABS/EPDM composites filled with graphene. *Composites Part B: Engineering* 83, 66–74.
- Xu, Y., Bai, H., Lu, G., Li, C., Shi, G., 2008. Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets. *Journal of the American Chemical Society* 130 (18), 5856–5857.
- Yang, H., Hernandez, Y., Schlierf, A., *et al.*, 2013. A simple method for graphene production based on exfoliation of graphite in water using 1-pyrenesulfonic acid sodium salt. *Carbon* 53, 357–365.
- Zhao, J.G., Xing, B.Y., Yang, H., *et al.*, 2016. Growth of carbon nanotubes on graphene by chemical vapor deposition. *New Carbon Materials* 31 (1), 31–36.
- Zhou, M., Tian, T., Li, X., *et al.*, 2014. Production of graphene by liquid-phase exfoliation of intercalated graphite. *International Journal of Electrochemical Science* 9, 810–820.

Further Reading

- Buerschaper, R.A., 1944. Thermal and electrical conductivity of graphite and carbon at low temperatures. *Journal of Applied Physics* 15 (5), 452–454.
- Graphite Mineral Data. Available at: <https://www.webmineral.com/data/Graphite.shtml#.WTepQuuGPIU>.
- Mindat. Available at: <https://www.mindat.org/min-1740.html>.
- NPTEL. Available at: [www.http://nptel.ac.in/courses/122103010/10](http://nptel.ac.in/courses/122103010/10).

Relevant Websites

www.mindat.org

Mindat.

www.webmineral.com

Mineralogy Database.

[www.http://nptel.ac.in/courses/122103010/10](http://nptel.ac.in/courses/122103010/10)

NPTEL.

PLA Composite Matrix as Functional Prototypes for Four Dimensional Applications

Sudhir Kumar, Thapar Institute of Engineering and Technology, Patiala, India

Rupinder Singh, Guru Nanak Dev Engineering College, Ludhiana, India

Tajinder P Singh and Ajay Batish, Thapar Institute of Engineering and Technology, Patiala, India

© 2019 Elsevier Inc. All rights reserved.

This is a reproduction of Sudhir Kumar, Rupinder Singh, Tajinder P. Singh, Ajay Batish, PLA Composite Matrix as Functional Prototypes for Four Dimensional Applications, In Reference Module in Materials Science and Materials Engineering, Elsevier Inc., 2019, doi:10.1016/B978-0-12-803581-8.11595-4.

Introduction

Three-dimensional (3D) printing also commonly known as additive manufacturing (AM) was commercially introduced in late 1980s. This is used to print 3D models of intricate designs. Significant studies have been reported on development of various 3D printing techniques but still lot of research in these technologies is required for making 3D technologies more cost effective (Khoo *et al.*, 2015; Kumar *et al.*, 2018). Product development cycle, less human interaction, and easy production of intricate models at low cost and value-added products are the major advantages in 3D printing techniques (Wong and Hernandez, 2012). 3D printing is yet not fully accepted technique for manufacturing especially for mass production but scientists, researchers, artists, medical practitioners use this technique for various applications (Flowers and Moniz, 2002; Noorani, 2006; Singh *et al.*, 2019). Metal powders, thermoplastics, natural fibers, reinforced matrix of polymers and various composites are some generally used materials for 3D printing (Tofail *et al.*, 2018).

Fig. 1 gives the various processes in AM which is basically categorized for liquid base, solid based, and powder based technologies (Kruth, 1991).

AM used for printing polymeric components can give better alternatives in the following manners (Ligon *et al.*, 2017):

- Low cost component production.
- Low weight components manufacturing.
- Easy production of intricate designs.
- Easy modifications in dimensions of components.

Study reveals that PLA itself behaves as smart material when worked near to its glass transition (T_g) temperature and is used as smart fiber when reinforced with nylon fibers for textile industry. Melt blown technique have been used by researcher to prepare composite of PLA and Fe_3O_4 (Leist *et al.*, 2017). Fig. 2(a) and (b) shows that addition of Fe_3O_4 to PLA does not alter the T_g of PLA but shifts the cold crystallization temperature to the positive side (Yu *et al.*, 2017).

Their results have also shown that when iron oxide is mixed and product is prepared the resulted product holds some amount of magnetic property in compare to neat PLA. Though the magnetic properties obtained via vibration sample magnetometer (VSM) testing were very less. Fig. 3 shows the hysteresis loop of PLA and Fe_3O_4 which shows that the composite behaves as paramagnetic composite.

4-D Printing

4D (4-dimensional) printing is not a new technique of printing but is an expansion of 3D printing. "Time" is the 4th dimension which is added to the previously known 3D printing technology. External triggering using some atmospheric change such as electric field, magnetic field, osmosis based actuation, and light based actuation etc. Thus in this technique of printing, a new composite filament is printed using FDM and the obtained product when triggered with some stimulus such as temperature, magnetic field, humidity and electric field, etc can changes its property respectively. This ability of changing shape and property at some future point of time after solidification of composite crystals comes from the highly engineered molecular spatial distributions and micro molecular smart reinforcement (Li *et al.*, 2016).

Types of 4-D printing

4-Dimensional printing may be defined as a printing of smart material which can respond to some external or internal stimulus at some required time of application. This response of component can be categorized in two types autonomous (without any external stimulus) and non-autonomous (with the help of external stimulus). Recently smart materials are one of the most important research area in which researchers are exploring. These smart materials can be used for 3D printing replacing the usual materials of printing. Thus incorporation of these smart materials in 3D printing is known as 4D printing which can be used to print various smart products. Once the fabricated product gets solidified as 3D object it can respond to external stimulus by using human interference that results in change of shape or physical properties over time (Khoo *et al.*, 2015).

Smart Materials

Smart materials can be of three types

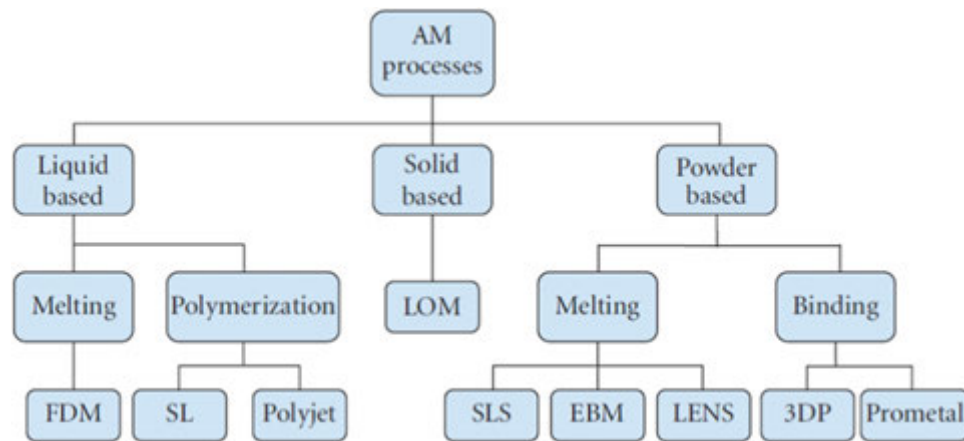


Fig. 1 3D printing processes. FDM: Fused deposition modeling, LENS: Laser engineered net shaping, SLS: Selective laser sintering, SL: Stereo lithography, EBM: Electron beam melting, LOM: Laminated object manufacturing. Reproduced from Kruth, 1991. Material increase manufacturing by rapid prototyping techniques. CIRP Annals 40 (2), 603–614. doi:10.1016/s0007-8506(07)61136-6.

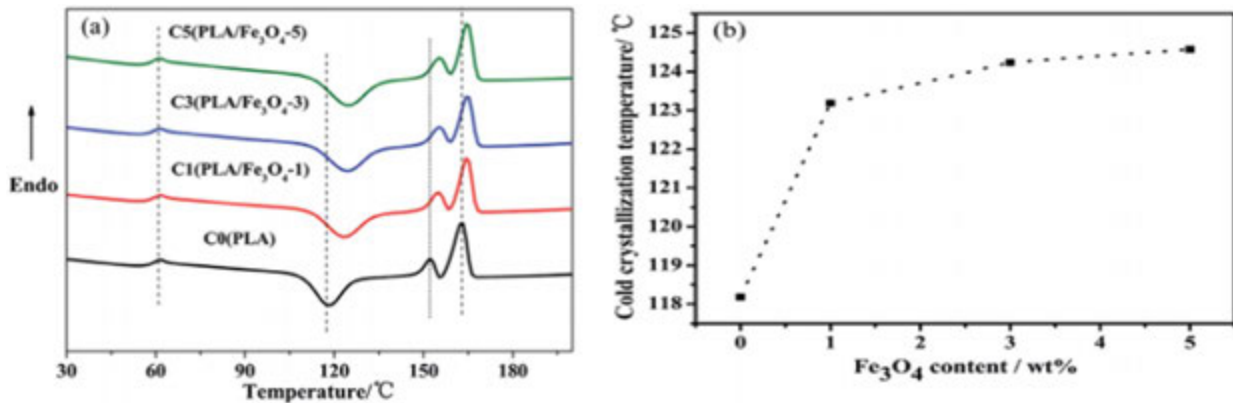


Fig. 2 Effect of Fe₃O₄ on PLA (a) effect on T_g (b) effect on T_{cc} (cold crystallization temperature). Reproduced from Yu, B., Wang, M., Sun, H., et al., 2017. Preparation and properties of poly (lactic acid)/magnetic Fe₃O₄ composites and nonwovens. RSC Advances 7 (66), 41929–41935.

- (1) Shape memory polymer (SMP): these polymers are naturally smart. There is no need for reinforcement to make them respond or to memorize their shape while triggered by some external stimulus (Zhou and Sheiko, 2016).
- (2) Shape changing polymer (SCP): these polymers can change their shape based on some external actuation but cannot memorize the shape. They remain in changed shape till they are triggered with external stimulus but as the external stimulus is off they come back to their original shape (Zhou and Sheiko, 2016).
- (3) Meta-materials: this category of smart components is one of those specially designed components which show change in property due to inherent printed geometry by 3D printing (Ge et al., 2014).

Programming Techniques for Smart Behavior

1.3.1 One step programming

One step programming means a component is coded in a way that it can respond to only one stimulus particularly and can change its shape for one stage and to make it to its original shape one have to apply another stimulus as represented in Fig. 2(a) (Hager et al., 2015).

Two step programming

As in the case of one step programming there was a restriction that the material cannot regain its shape without external stimulus application but in two step coded material the composite can regain its shape with the same stimulus by making on and off to the stimulus as shown in Fig. 2(b) (Hager et al., 2015).

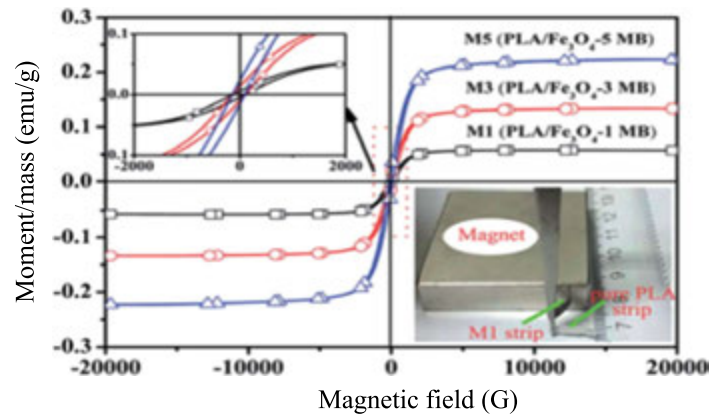


Fig. 3 Hysteresis loop of PLA with Fe_3O_4 . Reproduced from Yu, B., Wang, M., Sun, H., *et al.*, 2017. Preparation and properties of poly (lactic acid)/magnetic Fe_3O_4 composites and nonwovens. RSC Advances 7 (66), 41929–41935.

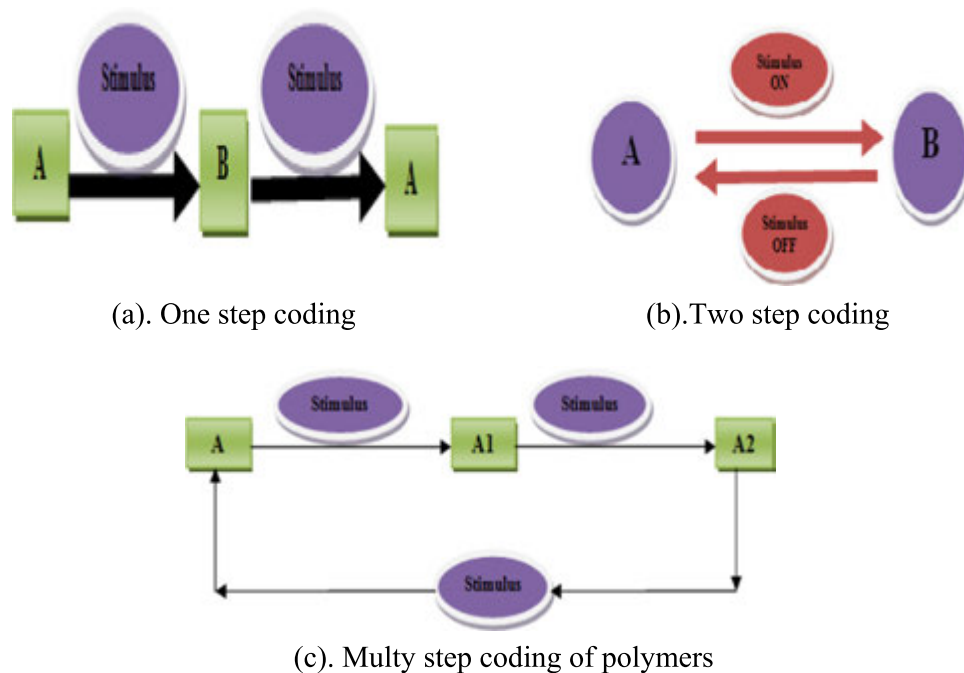


Fig. 4 (a). One step coding. (b). Two step coding. (c). Multy step coding of polymers.

Multy step coding of polymers

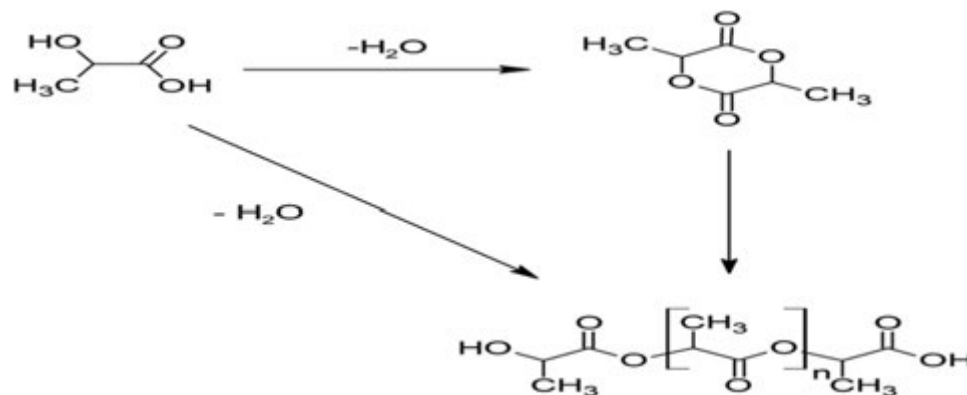
Coding of material for more than two stages with different or same stimulus is particularly known as multy step memory coding (Hager *et al.*, 2015). **Fig. 4(c)** shows the multy step coding of material.

Various Techniques and Smart Material Used for 3D Printing

Table 1 shows the diverse range of techniques applied for 3D printing for e.g., stereo lithography (SL), digital light processing (DLP), sacrificial mold technique (SMT), fused deposition modeling (FDM) and direct wire printing (DWP). Though DWP and SL is the most familiar techniques used in printing smart materials (Mu *et al.*, 2017; Cui *et al.*, 2016a,b; Borrello *et al.*, 2018; Nowicki *et al.*, 2016; Yang *et al.*, 2015; Mao *et al.*, 2016; Kutikov *et al.*, 2014; Singh *et al.*, 2019; Wu *et al.*, 2016).

Table 1 Different technology and materials for 3D printing

Technique	Material	Application
SL (stereo lithography)	Hydrogels such as Agarose and alginate, methacrylated hyaluronic acid and Soyabean oil epoxidized acrylate, etc.	Scaffolds for biomedical applications
Digital light processing (DLP)	Ethylene glycol phenyl ether acrylate (EGPEA), photo-curable methacrylate-based copolymer networks, photo-curable resin with multi-walled carbon nanotubes (MWCNTs), Polycaprolactone dimethacrylates	Tracheal stent for biomedical field
FDM (Fused deposition modeling)	PLA, poly (D, L-lactic acid-co-ethylene glycol-co-D, Hydroxyapatite, Polyurethane HA-PELA and L-lactic acid) (PELA) composites	Smart 4D filaments
DWP (Direct write printing)	Glassy shape memory polymer and Tangoblack1 and VeroWhite1 PLA, dichloromethane and benzophenone	Self-folding and expansion Self-folding and expansion
Sacrificial mold technique	PLA and Poly vinyl alcohol (PVA)	Self-folding and expansion

**Fig. 5** Structure of PLA with two roots.

Research Gaps

Based on literature review, gaps have been identified:

- Many researchers have explored the printing via FDM for commercially available materials, but very few have worked on thermo-sensitive and magneto-sensitive filament for 4D applications. In other words, the filament developed is sensitive for actuation with stimulus either heat, magnetic field or both. The 4D printing is upcoming field in AM and not much data has been reported regarding the 4-D printing with FDM (which is one of the low-cost AM techniques). Further it has been observed that very less has been reported on thermal and magnetic actuation together.
- PLA in combination of PVC reinforcement is very less studied which may be used as waste management of polymers as waste PVC can be reinforced into matrix of PLA.
- Smart materials are used in actuators, sensors applications and can be fabricated by conventional manufacturing processes as well as by 3D printing. Some of the commonly reported smart materials are PLA, magnetite powder. Still no work has been reported for preparing 4D printed parts by using PLA, PVC, Wood Dust and Magnetite powder with FDM process.

Proposed Material and Working Mechanism

PLA

PLA is a thermoplastic of semi crystalline nature in which crystalline structure as well as amorphous structure is present in some mixture. The glass transition temperature of PLA lies between the range of 58–60°C and melting temperature (T_m) varies between the range of 150–220°C (Martin and Avérous 2001; Jing *et al.*, 2014). PLA a biodegradable thermoplastic and bioactive thermoplastic is aliphatic polyester derived from resources which are renewable such as cassava roots, corn starch, and sugarcane in

Table 2 Mechanical properties of PLA

Properties	Values with respective units
Crystalline nature	Semi crystalline, 0%–37% Amorphous
Young modulus	1.2–3 GPa
Melting temperature	145–186°C
Glass transition temperature	50–64°C
Elongation at break	2%–6%
Tensile strength	28–50 MPa

**Fig. 6** PVC polymerization.

different parts of world. In 2010 PLA had the second largest consumption volume of any bio plastics of the world (see “Relevant Website section”). **Fig. 5** shows the basic structure of PLA which can be made through two available routes (Södergård and Stolt, 2010):

Using metal as catalysts with Ring opening polymerization of lactide

(1) Esterification

Table 2 shows the mechanical properties of poly lactic acid (PLA) (Mark, 1999) which are important from the research point of view.

PVC

Polyvinyl chloride (PVC) polymer which is a thermoplastic is the commonly available plastic polymer which have insulating as well as fire resisting property due to which it finds application in most of the electronic components such as cable, wires (Zabłocka-Malicka *et al.*, 2015; Yang *et al.*, 2007). Polyvinyl chloride is produced by polymerization of the vinyl chloride monomer (VCM) (Chanda and Roy, 2006), as shown by **Fig. 6**.

Wood Dust

Wood dust, which is of micro size is generated in the dealing of wood for different range of applications, is a complex substance. Composition of wood dust is totally dependent over the type of wood used for the particular application. Cellulose (approximately 40%–50%), is the main component of wood dust, other substances such as lignin, polyoses and a large and different number of molecules of low molecular mass which can alter the properties of wood. These low molecular mass components include non-polar organic extractives (waxes, resin acids, glycerides, terpenes, alcohols, steryl esters, sterols and fatty acids), polar organic extractives (quinones, lignans, flavonoids and tannins) and extractives which are water soluble (inorganic material, alkaloids, proteins and carbohydrates) (IARC, 1995).

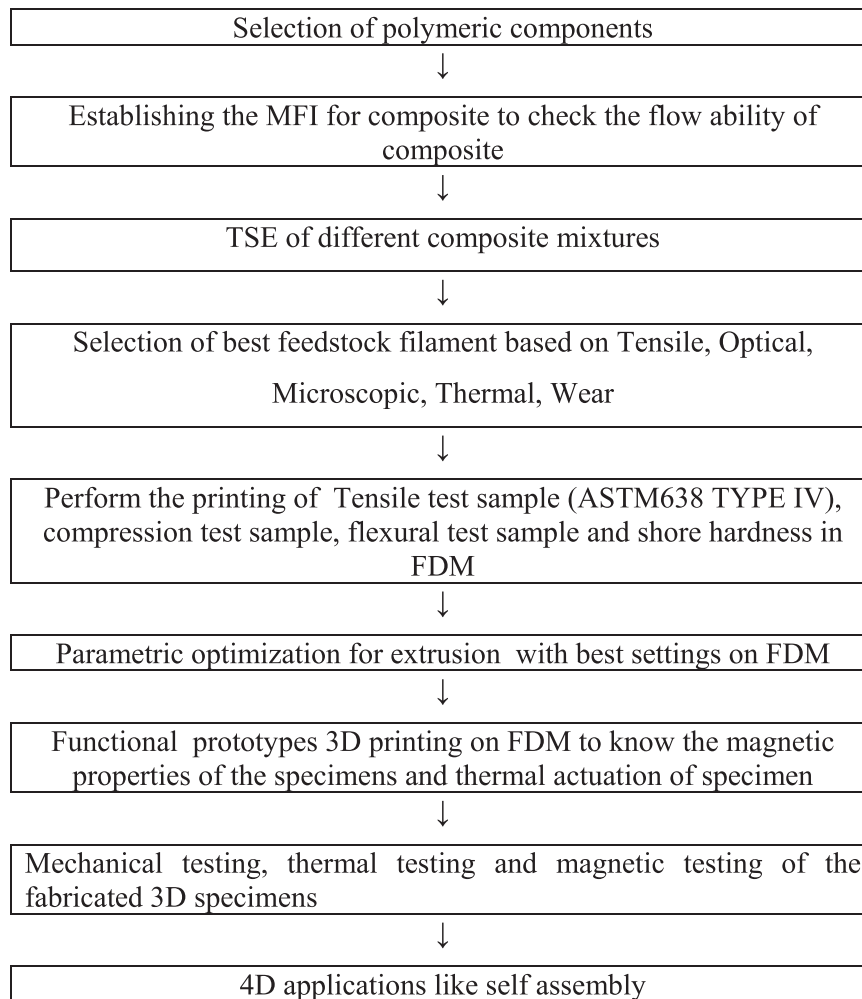
Magnetite Powder (Fe₃O₄)

Study reveals that Iron oxide generally found in three composite structure such as FeO, Fe₂O₃ (hematite) and Fe₃O₄ (magnetite). The FeO exists as a rock salt structure and is having anti-ferromagnetic behavior at low temperature. Fe₂O₃ (hematite) is having corundum structure and anti-ferromagnetic behavior. Fe₃O₄ possess spinal-structure as well as holds ferromagnetic order a corundum structure and an essentially anti-ferromagnetic order (Shiroishi *et al.*, 2003).

Table 3 provides the different properties of different Iron oxides which are further considered for material selection for research purpose (Cornell and Schwertmann, 2003).

Table 3 Properties of different iron oxide

Property	Hematite	Magnetite	Maghemite
Molecular formula	Alpha-Fe ₂ O ₃	Fe ₃ O ₄	Gamma-Fe ₂ O ₃
Density (g/cm ³)	5.26	5.18	4.87
Hardness	6.5	5.5	5
Type of magnetism	Weakly ferromagnetic or anti-ferromagnetic	Ferromagnetic	Ferri-magnetic
Curie temperature (K)	956	850	820–986
Crystallographic system	Rhombohedral	Hexagonal Cubic	Cubic or tetrahedral
Structural type	Corundum	Inverse spinal	Defect spinal

**Fig. 7** Proposed methodology for in-house fabrication of 4D feedstock filament.**Twin-Screw Extrusion (TSE)**

Cletral, 20 year back pioneered the “Twin screw extrusion” process for continuous production of uniform and finely structure components. Feed stock filament for 3D FDM printers, processing of different type of bio-plastics, thermoplastics etc. are some of the uses of TSE. Blending of different proportions of composite and giving a good quality product with good process control of machine conditions is the primary benefit of TSE. Different parametric conditions can be used with

Table 4 Composition of mixture

Serial no.	Polymers and reinforcements	Weight in grams (g)	Percentage of granules in composite mixture (%)
1	PLA	20	50
	PVC	10	25
	Magnetite powder (Fe_3O_4) (44 μm)	8	20
	Wood dust (50 μm)	2	5
2	PLA	21	52.5
	PVC	6	15
	Magnetite powder (Fe_3O_4) (44 μm)	10	25
	Wood dust (50 μm)	3	7.5
3	PLA	20	50
	PVC	9	22.5
	Magnetite powder (Fe_3O_4) (44 μm)	7	17.5
	Wood dust (50 μm)	4	10

**Fig. 8** Feedstock filaments for three proportions.**Table 5** Magnetic property values for the three extruded filaments

Sl. no.	Magnetic properties	Composition		
		Composition 1	Composition 2	Composition 3
1	Magnetization (emu/cm^3)	0.184	0.228	0.154
2	Coercivity (H_c) (Oersted(Oe))	72.36	74.97	76.88
3	Retentivity (M_r) (Tesla (T) or Gauss (G))	8.88E – 03	1.12E – 02	7.93E – 03

machine depending on requirement of design of experiment's which is provided by machine such as wide range of temperature, torque, rotation, and variable size of component. The basic benefit of using TSE is its different blending in bulk that gives the precise product output. In TSE process, the raw materials could be granules, solid particles, and powder or mixture of any of them (Dombe *et al.*, 2015).

Methodology

Fig. 7 shows the methodology adopted for the present study which clearly shows stepwise method to prepare a 4D feedstock filament for FDM applications.

Magnetostrictive Polymer Composite 4D Feedstock Filament: A Case Study

4D feedstock filament preparation for 3D printing is a precursor to the present study. It is necessary to have a proper mixture ratio of polymers and reinforcement so that the prepared feedstock filament can be used in fused deposition

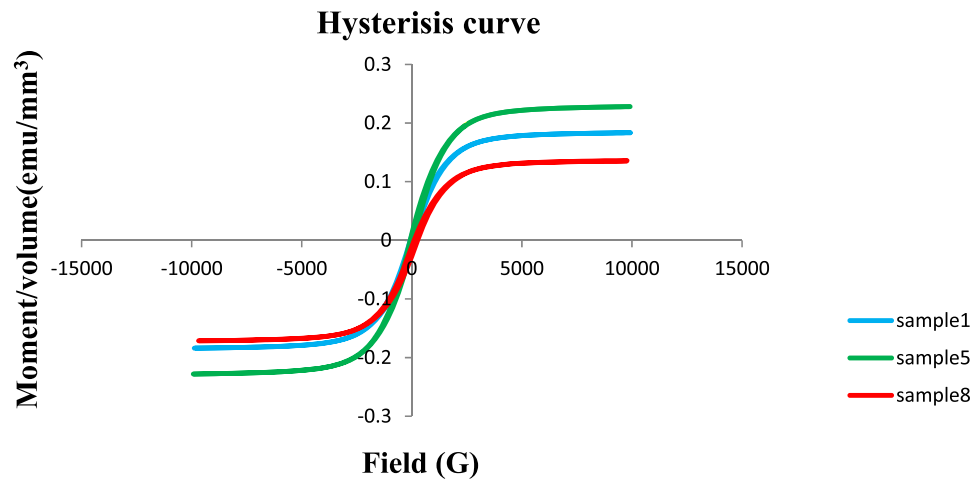


Fig. 9 Hysteresis loop for three filaments.

modeling (FDM). Therefore with repeated number of trials 3 composite mixture ratio is selected for better flowability (without choking of die), for precise size of obtained filament (diameter 1.7–1.75 mm) and for ease of extrusion with twin screw extrusion machine. **Table 4** shows all the selected composition with their percentage in the composite for the purpose of extrusion.

Fig. 8 shows the filaments for the three mixtures given in **Table 4** which shows that the given proportion is totally workable with twin screw extrusion machine and it was easy to obtain proper size of filaments with these taken mixture ratios.

For 4D properties, the obtained filaments also possess some magnetic property which is ensured by vibration sample magnetometer testing (VSM) which was performed by LAKESHORE model VSM machine having range of 1.5 tesla (T). The obtained value of magnetization (emu/volume), retentivity (tesla (T)) and coercivity (Oersted (Oe)) are given in **Table 5**.

Fig. 9 shows the hysteresis loop of the three filaments obtained by twin screw extrusion which clearly shows that there is some magnetic property in the filaments which necessary for 4D application such as self assembly.

Summary

In this article, a frame work for preparing in-house 4D feedstock filament with 3D printing has been proposed. This route will lead to development of customized 4D feedstock's filament for 4D properties that will ultimately lead to some attractive attributes such as:

- The preparation of various proportions of magnetite powder, PLA, PVC and wood dust for 4D applications and preparation of FDM feed stock filament (for commercial open source 3D printer) of magnetite powder, wood-dust, PLA and PVC by mixing with TSE.
- Establishing rheological (melt flow index), thermal properties for the filaments prepared by TSE and preparation of thermal actuation analysis data followed by parametric optimization of feedstock filament wire based upon metallurgical testing and mechanical (tensile test, scanning electron microscope) and selection of best feed stock filament For 4D capabilities.
- Parametric optimization of filament wire based upon vibration sample magnetometer (VSM) and selection of best wire filament condition needs to be performed. Finally printing of functional prototypes using FDM with best feedstock filaments and optimized data for best setting conditions based upon XRD, FTIR DMA data for best setting wire filaments and for printed components.

Acknowledgment

The author is highly obliged to GNDEC manufacturing lab and TIET providing labs to perform the current investigation.

References

- Borrello, J., Nasser, P., Latridis, J., Kevin, , 2018. 3D printing a mechanically-tunable acrylate resin on a commercial DLP-SLA printer. *Additive Manufacturing* 23, 374–380. doi:10.1016/j.addma.2018.08.019.
- Chanda, M., Roy, S.K., 2006. *Plastics Technology Handbook*. CRC Press. pp. 1–6. (ISBN 978-0-8493-7039-7).

- Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, second ed. Weinheim: Wiley-VCH.
- Cui, H., Zhu, W., Holmes, B., Zhang, L.G., 2016a. Biologically inspired smart release system based on 3D bioprinted perfused scaffold for vascularized tissue regeneration. *Advanced Science* 3 (8), 1600058. doi:10.1002/advs.201600058.
- Cui, H., Zhu, W., Nowicki, M., *et al.*, 2016b. Hierarchical fabrication of engineered vascularized bone biphasic constructs via dual3D bioprinting: Integrating regional bioactive factors into architectural design. *Advanced Healthcare Materials* 5 (17), 2174–2181. doi:10.1002/adhm.201600505.
- Dombe, G., Mehilal, D., Bhongale, C., Singh, P.P., Bhattacharya, B., 2015. Application of twin screw extrusion for continuous processing of energetic materials. *Central European Journal of Energetic Materials* 12 (3), 507–522.
- Flowers, J., Moniz, M., 2002. Rapid prototyping in technology education. *Technology Teacher* 62 (3), 7–11. Retrieved January 2, 2019 from <https://www.learntechlib.org/p/95508/>
- Ge, Q., Dunn, C.K., Qi, H.J., Dunn, M.L., 2014. Active origami by 4D printing. *Smart Materials and Structures* 23 (9), doi:10.1088/0964-1726/23/9/094007.
- Hager, M.D., Bode, S., Weber, C., Schubert, U.S., 2015. Shape memory polymers: Past, present and future developments. *Progress in Polymer Science* 49–50, 3–33. doi:10.1016/j.progpolymsci.2015.04.002.
- IARC, 1995. Wood Dust and Formaldehyde. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. 62. WHO Press. pp. 1–405.
- Jing, X., Mi, H.-Y., Peng, X.-F., Turng, L.-S., 2014. The morphology, properties, and shape memory behavior of polylactic acid/thermoplastic polyurethane blends. *Polymer Engineering & Science* 55 (1), 70–80. doi:10.1002/pen.23873.
- Khoo, Z.X., Teoh, J.E.M., Liu, Y., *et al.*, 2015. 3D printing of smart materials: A review on recent progresses in 4D printing. *Virtual and Physical Prototyping* 10 (3), 103–122. doi:10.1080/17452759.2015.1097054.
- Kruth, J.P., 1991. Material increment manufacturing by rapid prototyping techniques. *CIRP Annals* 40 (2), 603–614. doi:10.1016/S0007-8506(07)61136-6.
- Kumar, R., Singh, R., Ahuja, I., 2018. Friction stir welding of ABS-15Al sheets by introducing compatible semi-consumable shoulder-less pin of PA6-50Al. *Measurement* 131, 461–472. doi:10.1016/j.measurement.2018.09.005.
- Kutikov, A.B., Reyer, K.A., Song, J., 2014. Shape-memory performance of thermoplastic amphiphilic triblock copolymer poly (d,l-lactic acid-co-ethylene glycol-co-d,l-lactic acid) (PELA)/hydroxyapatite composites. *Macromolecular Chemistry and Physics* 215 (24), 2482–2490. doi:10.1002/macp.201400340.
- Leist, S.K., Gao, D., Chiou, R., Zhou, J., 2017. Investigating the shape memory properties of 4D printed polylactic acid (PLA) and the concept of 4D printing onto nylon fabrics for the creation of smart textiles. *Virtual and Physical Prototyping* 12 (4), 290–300. doi:10.1080/17452759.2017.1341815.
- Li, Y.-C., Zhang, Y.S., Akpek, A., Shin, S.R., Khademhosseini, A., 2016. 4D bioprinting: The next-generation technology for biofabrication enabled by stimuli-responsive materials. *Biofabrication* 9 (1), 012001. doi:10.1088/1758-5090/9/1/012001.
- Ligon, S.C., Liska, R., Stampfl, J., Gurr, M., Mülhaupt, R., 2017. Polymers for 3D printing and customized additive manufacturing. *Chemical Reviews* 117 (15), 10212–10290. doi:10.1021/acs.chemrev.7b00074.
- Mao, Y., Ding, Z., Yuan, C., *et al.*, 2016. 3D printed reversible shape changing components with stimuli responsive materials. *Scientific Reports* 6 (1), doi:10.1038/srep24761.
- Mark, J.E., 1999. Poly (lactic acid). In: Mark, J.E. (Ed.), *Polymer Data Handbook*. New York: Oxford University Press, pp. 627–633.
- Martin, O., Avérous, L., 2001. Poly (lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymer* 42 (14), 6209–6219. doi:10.1016/S0032-3861(01)00086-6.
- Mu, Q., Wang, L., Dunn, C.K., *et al.*, 2017. Digital light processing 3D printing of conductive complex structures. *Additive Manufacturing* 18, 74–83. doi:10.1016/j.addma.2017.08.011.
- Noorani, R., 2006. *Rapid Prototyping: Principles and Applications*. Wiley. (ISBN-10: 0471730017).
- Nowicki, M.A., Castro, N.J., Plesniak, M.W., Zhang, L.G., 2016. 3D printing of novel osteochondral scaffolds with graded microstructure. *Nanotechnology* 27 (41), 414001. doi:10.1088/0957-4484/27/41/414001.
- Shiroishi, H., Oda, T., Hamada, I., Fujima, N., 2003. Structure and magnetism on iron oxide clusters Fe_nO_m ($n = 1-5$): Calculation from first principles. *The European Physical Journal D – Atomic, Molecular and Optical Physics* 24 (1–3), 85–88. doi:10.1140/epjd/e2003-00136-3.
- Singh, R., Kumar, R., Farina, I., *et al.*, 2019. Multi-material additive manufacturing of sustainable innovative materials and structures. *Polymers* 11 (1), 62. doi:10.3390/polym11010062.
- Södergård, A., Stolt, M., 2010. Industrial production of high molecular weight poly (lactic acid). In: Auras, R.A., Lim, L.-T., Selke, S.E.M., Tsuji, H. (Eds.), *Poly (Lactic Acid) Synthesis, Structures, Properties, Processing, and Applications*. Wiley, pp. 27–41.
- Tofail, S.A.M., Koumoulos, E.P., Bandyopadhyay, A., *et al.*, 2018. Additive manufacturing: Scientific and technological challenges, market uptake and opportunities. *Materials Today* 21 (1), 22–37. doi:10.1016/j.mattod.2017.07.001.
- Wong, K.V., Hernandez, A., 2012. A review of additive manufacturing. *ISRN Mechanical Engineering*. 1–10. doi:10.5402/2012/208760.
- Wu, J., Yuan, C., Ding, Z., *et al.*, 2016. Multi-shape active composites by 3D printing of digital shape memory polymers. *Scientific Reports* 6 (1), doi:10.1038/srep24224.
- Yang, L., Hu, Y., You, F., Chen, Z., 2007. A novel method to prepare zinc hydroxystannate-coated inorganic fillers and its effect on the fire properties of PVC cable materials. *Polymer Engineering & Science* 47 (7), 1163–1169.
- Yang, Y., Chen, Y., Wei, Y., Li, Y., 2015. 3D printing of shape memory polymer for functional part fabrication. *The International Journal of Advanced Manufacturing Technology* 84 (9–12), 2079–2095. doi:10.1007/s00170-015-7843-2.
- Yu, B., Wang, M., Sun, H., *et al.*, 2017. Preparation and properties of poly (lactic acid)/magnetic Fe_3O_4 composites and nonwovens. *RSC Advances* 7 (66), 41929–41935. doi:10.1039/c7ra06427f.
- Zablocka-Malicka, M., Rutkowski, P., Szczepaniak, W., 2015. Recovery of copper from PVC multiwire cable waste by steam gasification. *Waste Management* 46, 488–496.
- Zhou, J., Sheikh, S.S., 2016. Reversible shape-shifting in polymeric materials. *Journal of Polymer Science Part B: Polymer Physics* 54 (14), 1365–1380. doi:10.1002/polb.24014.

Further Reading

- Caresana "Bioplastics-Study: Market, Analysis, Trends-coresana". Available at: www.caresana.com. Archived from the original on 4 November 2017. Retrieved 9 May 2018.
- Ge, Q., Sakhaei, A.H., Lee, H., *et al.*, 2016. Multimaterial 4D printing with tailorable shape memory polymers. *Scientific Reports* 6 (1), doi:10.1038/srep31110.
- Gu, X., Mather, P.T., 2012. Entanglement-based shape memory polyurethanes: Synthesis and characterization. *Polymer* 53 (25), 5924–5934. doi:10.1016/j.polymer.2012.09.056.
- Mao, Y., Yu, K., Isakov, M.S., *et al.*, 2015. Sequential self-folding structures by 3D printed digital shape memory polymers. *Scientific Reports* 5 (1), doi:10.1038/srep13616.
- Singh, N., Singh, R., Ahuja, I.P.S., Farina, I., Fraternali, F., 2018. Metal matrix composite from recycled materials by using additive manufacturing assisted investment casting. *Composite Structures* 207, 129–135. doi:10.1016/j.compstruct.2018.09.072.

Singh, R., Sandhu, G.S., Penna, R., Farina, I., 2017. Investigations for thermal and electrical conductivity of ABS-graphene blended prototypes. *Materials* 10 (8), 881.

Singla, R.K., Zafar, M.T., Maiti, S.N., Ghosh, A.K., 2017. Physical blends of PLA with high vinyl acetate containing EVA and their rheological, thermo-mechanical and morphological responses. *Polymer Testing* 63, 398–406. doi:10.1016/j.polymertesting.2017.08.042.

Relevant Website

<http://www.ceresana.com/en/market-studies/plastics/bioplastics/>

Bioplastics Market Report: Industry Analysis, 2023
Ceresana.

Extrusion-Based Additive Manufacturing Techniques for Biomedical Applications

Ghazal Tadayyon, Trinity College Dublin, Dublin, Ireland

Daniel J Kelly and Michael G Monaghan, Trinity College Dublin, Dublin, Ireland; Advance Materials and BioEngineering Research (AMBER) Centre at Trinity College Dublin and the Royal College of Surgeons in Ireland, Dublin, Ireland; and Centre for Research in Medical Devices (CURAM), National University of Ireland, Galway, Ireland

© 2021 Elsevier Inc. All rights reserved.

List of Nomenclature

Base quantity	Unit	Symbol	
Length	Meter	m	
	Micrometer	μm	
	Nanometer	nm	
Derived quantity	Name	Symbol	Expression in terms of SI base units
Dynamic viscosity	pascal second	Pa s	$\text{kg m}^{-1} \text{s}^{-1}$
	Kilopascal second	kPa s	$10^3 \text{ kg m}^{-1} \text{s}^{-1}$
Youngs Modulus	Pascal	Pa	N m^{-2}
	Megapascal	MPa	N mm^{-2}

Introduction

Additive manufacturing (AM) is a promising technology for the generation of customized products and prototypes requiring geometrical complexity. Often interchangeably labeled as 3D printing; ISO/ASTM standards define 3D printing as the process of fusing or depositing materials such as polymers, metals, ceramics, and living cells, layer by layer to produce an architecture dictated from a digital CAD software file (Gibson *et al.*, 2014). AM has been utilized within many fields, one of which is the medical device industry, with the use of 3D printing in this field expanding rapidly to improve health care. In 2018, the 3D-printed medical devices market which is segmented into equipment (3D printers), materials and software & services; accounted for a value of US\$ 0.84 billion in 2017, and is projected to grow to US\$ 1.88 billion by 2022 at a Compound annual growth rate (CAGR) of 17.5% (Markets and Markets™, 2017). Other reports state that the global 3D printing healthcare market size, categorized as components, technologies and applications; in total was valued at US\$ 973 million in 2018, and is projected to reach US\$3.7 billion by 2026 growing at a CAGR of 18.2% from 2019 to 2026 (Allied Market Research, 2019). Europe will likely continue as a major stakeholder in the widespread fabrication of 3D-printed biomedical devices, indicated by market research that predicts Europe will double production by 2025–2029 (Future Market Insights, 2019).

The versatility and the opportunities 3D printing presents is being increasingly appreciated. With the 2019–2020 coronavirus pandemic; engineers and designers quickly turned to 3D printing to rapidly replenish a shortage of respiratory valves; whereby volunteers reverse engineered a patented valve to produce 100 3D-printed valves in 24 h at a cost of approximately US\$ 1 per unit (Healthcare IT News, 2020). In the same fashion, the i-Form research facility based in University College Dublin (UCD) Ireland, designed and manufactured face shields for frontline medical staff working with Covid-19 patients to hospitals in Dublin and to Health Service Executive (HSE) coronavirus testing centers around the greater Dublin area (The Irish Times, 2020). Moreover, to develop measures against the coronavirus crisis, a Belgium-based pioneer in 3D printing has created a non-invasive Positive End Expiratory Pressure (PEEP) mask Connector; a device to convert standard equipment available in most hospitals, into a mask to facilitate breathing for patients by creating positive pressure in the lungs (Materialise, 2020).

3D printing for biomedical applications can be categorized into engineered tissue and biofabrication (Zadpoor and Malda, 2017), surgical implants (Willemsen *et al.*, 2019), and drug delivery (Norman *et al.*, 2017). Tissue engineering merges the principles of materials and cell transplantation to develop substitute tissues and/or promote endogenous regeneration based on key engineering principles and typically utilizes biomaterial scaffolds as platforms to promote such regeneration and/or delivery therapeutic cells or biochemical factors to do so. Instinctively, tissue engineering has begun to employ 3D printing technology to fabricate such scaffolds and, in some cases, simultaneously print scaffolds, cells and biochemical factors together which can provide more scalable and reproducible medical solutions. With their development progressing at a rapidly growing rate, patient-specific 3D printed cell-laden products could positively influence the patient recovery time and therapeutic outcome (Mertz, 2013).

Furthermore, the pharmaceutical industry has adopted AM towards achieving more personalized medicine. AM technology allows printing specific doses on demand, with reduced cost, ease of use and desired drug release kinetics to improve patient care (Musarrat *et al.*, 2018). The ability to predesign geometries with desired release profiles and quantities by amending the CAD file is breaking new ground in the application of 3D printing for drug product development (Azad *et al.*, 2020).

From a materials point of view, currently approved AM technologies can be organized into seven categories; that of vat photopolymerization, powder-based, materials jetting, binder jet printing, materials extrusion, direct energy deposition and

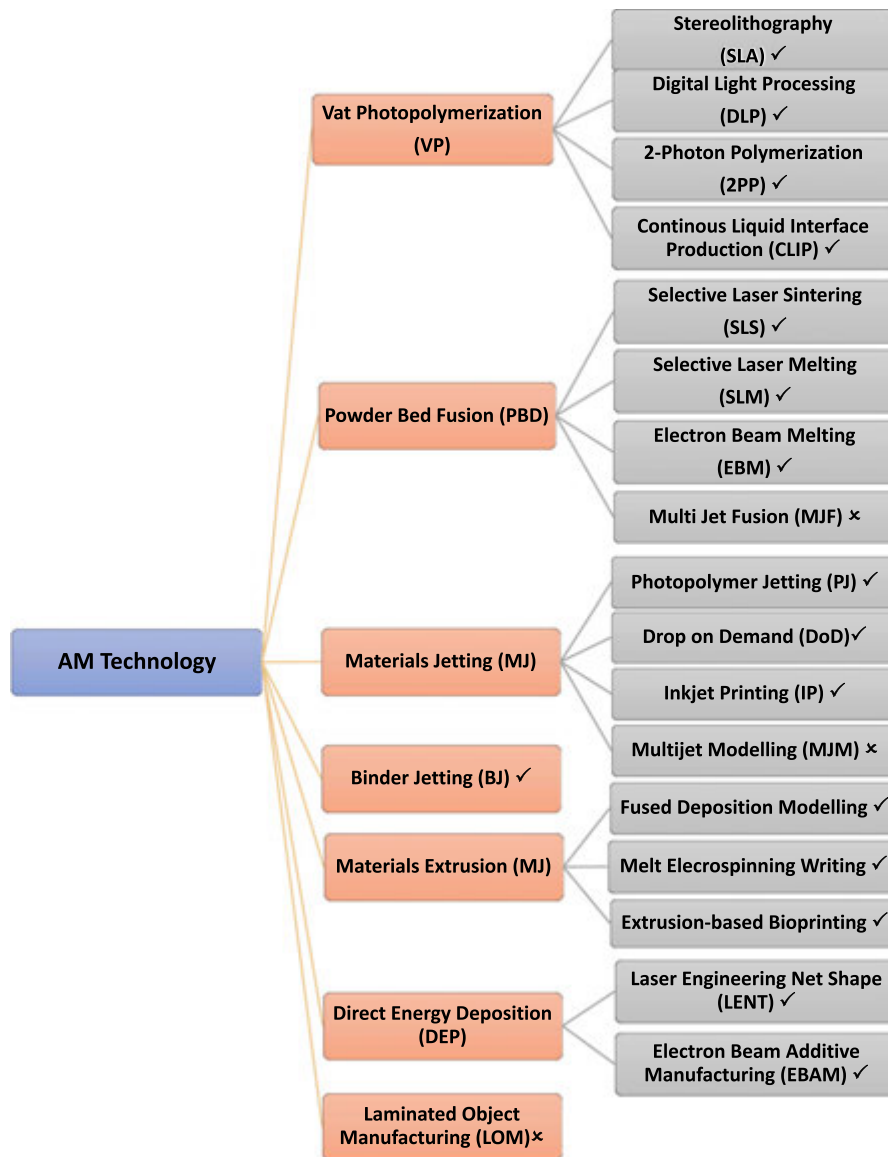


Fig. 1 Brief graphical abstract of common AM methods. The checkmarks apply to the technologies that (to the best of our knowledge) have been used for biomedical applications.

laminated object manufacturing (Lim *et al.*, 2018; Yang *et al.*, 2018a). These categories can be further expanded into the general available 3D printing technologies and are summarized in Fig. 1.

Photo-polymerization processes rely on selectively curing a liquid photopolymer under a radiation source of appropriate wavelength (Yang *et al.*, 2001). Powder bed fusion (PBF) is a subset of AM using a numerically controlled heat source, building a component layer-by-layer from a pre-placed powder (Goodridge and Ziegelmeier, 2017). Materials jetting process involves spraying a layer of photopolymer from hundreds of tiny nozzles while simultaneously curing the layer with UV light before printing the next layer (Kelly *et al.*, 2018). This technique is a useful choice for realistic prototypes, providing high resolution, accuracy and a smooth surface finish (Biglino *et al.*, 2013). Binder jetting is an alternative printing method placing powder layer by layer joining at the selective areas with a liquid binder. Laminated object manufacturing is an approach to create a part by lamination of sheet feedstock, which is laser-cut along contours instructed by an STL file-generated tool path (Safari *et al.*, 2001). In directed energy deposition technology, an electron or laser beam is used to melt and solidify the starting material which is supplied as a powder, filament or wire in a layer-wise pattern (Bose *et al.*, 2018).

Material extrusion 3D printing technology is perhaps one of the most popular AM methods for scaffold fabrication as it offers a wide range of printable biomaterials in terms of design and geometry and inexpensive equipment (Derakhshanfar *et al.*, 2018). Extrusion rapid prototyping methods can be categorized as fused filament fabrication (FFF) or its trademarked term fused deposition modeling (FDM™), melt-electrospinning writing, known as melt-electro writing (MEW), and extrusion-based

bioprinting (EBB). In this article, we will present the fundamentals of FDM, MEW and EBB and discuss biomaterial scaffolds and their application in tissue engineering and medical technologies. We also discuss emerging prospects in these fields to overcome current challenges and realize the next generation of 3D printing processes.

Fused Deposition Modeling (FDM™)

In 1992, Scott Crump secured a U.S. patent for an "apparatus and method for creating three-dimensional objects" (Crump, 1992). He termed the technology Fused Deposition Modeling (FDM). FDM concerns a thermoplastic filament extruded from a hot nozzle deposited as a semi-molten polymer in a layer by layer process (Zein *et al.*, 2002). This technique has generated an increased demand in rapid prototyping due to its simplicity, low cost, table-top sized equipment and low-risk processes which avoid the use environmentally hazardous solvents (Garzon-Hernandez *et al.*, 2020).

FDM can yield 3D structures with fully interconnected channel networks, and highly controllable porosity (Zein *et al.*, 2002). The stiffness, yield strength, flexural strength and therefore the quality of the 3D parts are influenced by the internal structure, pore sizes and shapes of the deposited materials (Dhinakaran *et al.*, 2020). Nowadays, various types of biomaterials are used with FDM, including pure polymers, copolymers, polymer blends and composites.

3D printed tissue engineered scaffolds can often be designed with complex configurations and highly interconnected pore structures to provide a suitable pore structure for cell attachment and proliferation, while retaining the required mechanical function (Hutmacher, 2001). Porous scaffolds with sufficient surface areas are often produced using traditional methods such as freeze drying, solvent casting, fiber meshes/fiber bonding, phase separation, and gas foaming. However, achieving customized scaffolds which are geometrically compatible with a patient's local anatomy with specific spatial patterning is one advantage of AM (Jariwala *et al.*, 2015).

For instance, much effort has focused on the fabrication of 3D fibrous structures for bone tissue engineering to produce mechanically competent implants that also provide a base for cell attachment and proliferation (Bendtsen *et al.*, 2017; Nyberg *et al.*, 2016). Cancellous bone is spongy in nature with a porosity ranging from 50 to 90 vol% (Bose *et al.*, 2013), in contrast to cortical or compact bone (which contributes more to the mechanical role of bone) having less than 10 vol% porosity (Fuchs *et al.*, 2019). Bone porosity can change with age, disease states and lifestyle (Fuchs *et al.*, 2019). On the basis of Magnetic Resonance Imaging (MRI) and micro computed tomography (μ -CT), the anatomic geometry of bones and/or their defects can be obtained and imported as a patient CAD model for scaffold fabrication at a microstructural level (Tavares and Natal, 2018). Porous structures have been designed and manufactured using FDM to achieve predefined porosity levels and pore sizes in order to promote osseointegration (Buj-Corral *et al.*, 2018). CT-guided FDM has also been reported in the fabrication of PCL/HA 3D bone scaffolds with both cortical and cancellous bone regions (Xu *et al.*, 2014). These reports demonstrated an appropriate in vivo biocompatibility, new bone formation and a predictive biodegradation rate which holds promise for future bone regenerative applications (Xu *et al.*, 2014). In another piece of work, the grafting of FDM-printed PEEK reinforced with carbon fiber was successfully fabricated yielding significant mechanical properties to be employed as the orthopedic and dental implant materials (Han *et al.*, 2019).

With regard to the 3D printing of drug loaded structures, antibiotic- and chemotherapeutic agents have been incorporated into PLA filaments which maintained mechanical integrity throughout the FDM process (Weisman *et al.*, 2015). This can offer patient-specific scaffold containing antibiotic treatment and/or drug delivery with a sustained-release capacity. Other reports have presented FDM fabricated polycaprolactone-tricalcium phosphate (PCL-TCP) meshes for the delivery of gentamicin sulfate (GS) to achieve an effective localized release when applied as a wound dressing, eliminating bacteria while still possessing appropriate biocompatibility with dermal fibroblasts (Teo *et al.*, 2011). Moreover, in vivo investigations have demonstrated that this platform (in particular PCL-15 wt% GS) operated as a highly effective local antibiotic delivery vehicle capable of eliminating bacterial infections within 7 days (Teo *et al.*, 2011). PCL filaments loaded with quinine produced by hot melt extrusion have also demonstrated tailored release profiles using this model drug in a proof-of-concept study (Kempin *et al.*, 2017). These studies demonstrate the capacity of FDM to produce customized implants with controlled drug delivery.

Despite the clear benefits of FDM, some limitations are present. These include filament temperature control which affects the viscosity of melted polymer, as well as the fabrication of functional interconnected network structures with an adequate surface area-to-volume ratio. Moreover, when 3D-printed materials require nano and micro reinforcement using ceramics, polymers or metal nanoparticles (Walmsley *et al.*, 2015), the porosity of FDM printed constructs can be even lower because a larger filament diameter is required to prevent clogging during the extrusion (Grottkau *et al.*, 2020). For instance, FDM fabrication of HA reinforced PLA scaffolds designed towards small bone defect replacement have been reported with a porosity of only 30% (Senatov *et al.*, 2016).

Melt Electro-Writing (MEW)

Recently, melt electrospinning technology has emerged as an approach to fabricate ultrafine fibers from polymer-based inks. MEW, as an electrohydrodynamic approach; deposits ultrathin fibers layer-by-layer on a stage (Farrugia *et al.*, 2013) or a mandrel (Jungst *et al.*, 2015) collector dictated by G-code commands to fabricate 3D textiles and scaffolds for tissue engineering (Dalton *et al.*, 2013). A melt electrospinning printer typically contains a static syringe heater which melts material and an applied air pressure forces polymer to

flow out through a spinneret which is linked to a high voltage source (Wunner *et al.*, 2017). A threshold voltage charges the polymer structure to generate a steady cone-jet structure. A high viscosity polymer with low conductivity results in a stable Taylor cone and straight melt flow to precisely deposit the continuous fiber (Farrugia *et al.*, 2013). Linear writing is possible when the collector speed is higher than critical translation speed in order to avoid oscillatory deposition of the fiber (Hochleitner *et al.*, 2016).

Fiber diameter and morphology can have a significant influence on cell behavior and mechanical performance of materials (Cardwell *et al.*, 2014). Therefore it is important to note that MEW, can achieve fiber diameters less than one micron; much smaller when compared to FDM which achieves on average a minimum diameter of 200 μm (Lam and Chen, 2019). Moreover, well-aligned MEW fibers at sub-micron diameter offer the benefit of desired structure in nano-level with reported fiber diameter of 292 nm produced from single collector and 270 nm for dual collector systems (Dalton *et al.*, 2007; Dalton *et al.*, 2006).

While 3D printing of polymer scaffolds is typically applied to hard tissues, MEW allows for the manufacture of small diameter ($> 20 \mu\text{m}$) fiber structures suitable for soft-tissue engineering (Robinson *et al.*, 2019), such as cartilage (Visser *et al.*, 2015), periosteum (Baldwin *et al.*, 2017), nerves (Petcu *et al.*, 2018), skin (Farrugia *et al.*, 2013), and cardiac tissue (Bas *et al.*, 2018). Producing such small diameter fibers enables the fabrication of engineered fibrous architectures similar to the native ECM (Eichholz and Hoey, 2018). MEW has been used to fabricate skin substitutes consisting of PCL scaffolds with 7.5 μm diameter fibers with interfiber distances of approximately 46 μm , facilitating fibroblasts to attach to and infiltrate through the melt-electrospun scaffolds both laterally and vertically to form a 3D cellularized construct (Farrugia *et al.*, 2013). MEW has also been used to produce tubular scaffolds whereby PCL tubes were fabricated by MEW depositing 20 μm diameter fibers at different winding angles and collecting on rotating cylinder (Brown *et al.*, 2012). These tubular scaffolds acted as provisional substitutes for ECM and demonstrate human osteoblast, mouse osteoblast and human mesothelial cell compatibility (Brown *et al.*, 2012).

MEW has also been used to create sacrificial PCL templates to achieve a hierarchical porous structure of poly(2-oxazoline) hydrogels (Haigh *et al.*, 2016). Such indirect printing of pore structures within hydrogels can provide highly defined hierarchical structures to control diffusion of nutrients, growth factors or pharmaceuticals.

Extensive z-direction mobility is avoided in the electrospinning field to avoid an excess charge becoming trapped within the deposited polymer in the region close the spinneret (Wunner *et al.*, 2018), which limits the height of scaffolds that can be produced using this technique. In an innovative approach to overcome this obstacle, a mechatronic system was designed to control the collector distance in a MEW set-up (Wunner *et al.*, 2018). This has enabled significantly thicker scaffolds (exceeding 7 mm) to be fabricated.

Hydrogels (alginate and methacrylated gelatin) reinforced with a highly organized porous network of PCL fabricated by MEW enabled the engineering of composites with similar compressive mechanical properties to that of native articular cartilage, without negatively impacting the capacity of the construct to support the deposition of a cartilage-like tissue by encapsulated cells (Visser *et al.*, 2015). Similar approaches have been used to reinforce PEG/heparin hydrogels (Bas *et al.*, 2017). In a cardiac application, melt-electrowritten constructs of a hydroxyl functionalized polyester have been designed to mimic the mechanical properties of the native myocardial tissue, whilst simultaneously promoting cardiac progenitor cell (CPC) alignment (Castilho *et al.*, 2017).

The main advantage of MEW is achieving highly precise constructs from ultrafine filaments which can be used to obtain complex designs for different applications in tissue engineering. One main drawback of MEW is the hydrophobic nature of the polymers commonly used in MEW due to their hydrocarbon backbones which prohibit cell adhesion and appropriate biocompatibility (Richbourg *et al.*, 2019; Shin *et al.*, 2003). Contingency for this is often post processing surface treatment of the relatively hydrophobic melt electrowritten fibers by plasma, NaOH treatment, or coating using a secondary polymer (Afghah *et al.*, 2019).

As demonstrated in Fig. 2, FDM scaffolds can have orderly and controlled geometries together with a low porosity which offers high level of biocompatibility (Li *et al.*, 2019), while multimodal MEW scaffolds possess highly-tunable geometry and superior level of porosity (Hrynevich *et al.*, 2018) (Fig. 3). Taken together, melt electro-writing provides fibrous scaffolds with smaller fiber diameters (and therefore higher overall porosity achievable) and designs at a higher resolution which is favorable for cell invasion and growth.

Extrusion-Based Bioprinting (EBB)

3D Bioprinting is concerned with a layer-by-layer, precise positioning of living cells, biomaterials, and active biomolecules to construct 3D structures (Murphy and Atala, 2014); with a focus on three approaches: biomimicry, autonomous self-assembly and mini-tissue building blocks (Murphy and Atala, 2014). Its most common form; extrusion-based bioprinting; is the extrusion of cell-laden hydrogels or 'bio-inks' onto printing stages, in a layer-by-layer fashion to form 3D platforms of various sizes, shapes and resolutions.

A major advantage of this process is the ability to print high cell densities at a high production (Rider *et al.*, 2018). However, its relatively low resolution in comparison with conventional 3D printing methods is a limitation of this method (Duan *et al.*, 2013).

Extrusion based bioprinting systems typically employ materials (hydrogel bioinks) with high viscosity, predetermined by the polymer concentration and molecular weight (e.g., viscosity of Lutrol® F 127 with 12 kDa molecular weight $\sim 600 \text{ kPa s}$). Therefore, 3D printing hydrogels often results in reduced accuracy and resolution (typically $> 100 \mu\text{m}$), and the final shape of 3D constructs often relies on crosslinking post-printing. Extrusion resolution can be enhanced by utilizing a smaller nozzle, though this comes at the cost of cell damage due to an increased shear force during printing (Chang *et al.*, 2008). Moreover, selecting the correct material is a must to achieve complex anatomical architectures with an appropriate degree of stiffness to preserve viability of embedded cells (Murphy and Atala, 2014).

One target for EBB based bioprinting is skin, which being the largest organ in the human body, provides protection from the external environment, regulates body temperature, and preserves body fluid. Extensive injuries, i.e., deep skin burns and chronic wounds, and

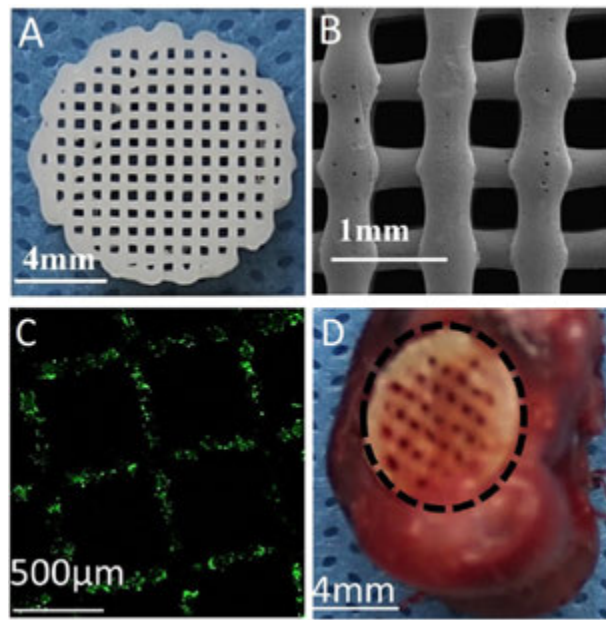


Fig. 2 Digital photograph, SEM, confocal laser scanning microscopy and Live/dead analysis of bone marrow-derived mesenchymal stem cells (BMSCs) cultured on PCL structures fabricated by FDM. (A) FDM printed structure of PCL scaffold 12 mm in diameter, 4 mm in height, 100% pore interconnectivity, 500 μm pore size, and 56% scaffold porosity, (B) Corresponding SEM image of the scaffold, (C) Confocal image of 3D PCL after being cultured for 7 days in vitro, (D) Formation of small amount of bone-like tissue with cells attachment to the fibers and proliferated within the pores after 4 weeks in vivo. Adapted from Li, J., Li, L., Zhou, J., *et al.*, 2019. 3D printed dual-functional biomaterial with self-assembly micro-nano surface and enriched nano argentine for antibacterial and bone regeneration. *Applied Materials Today* 17, 206–215.

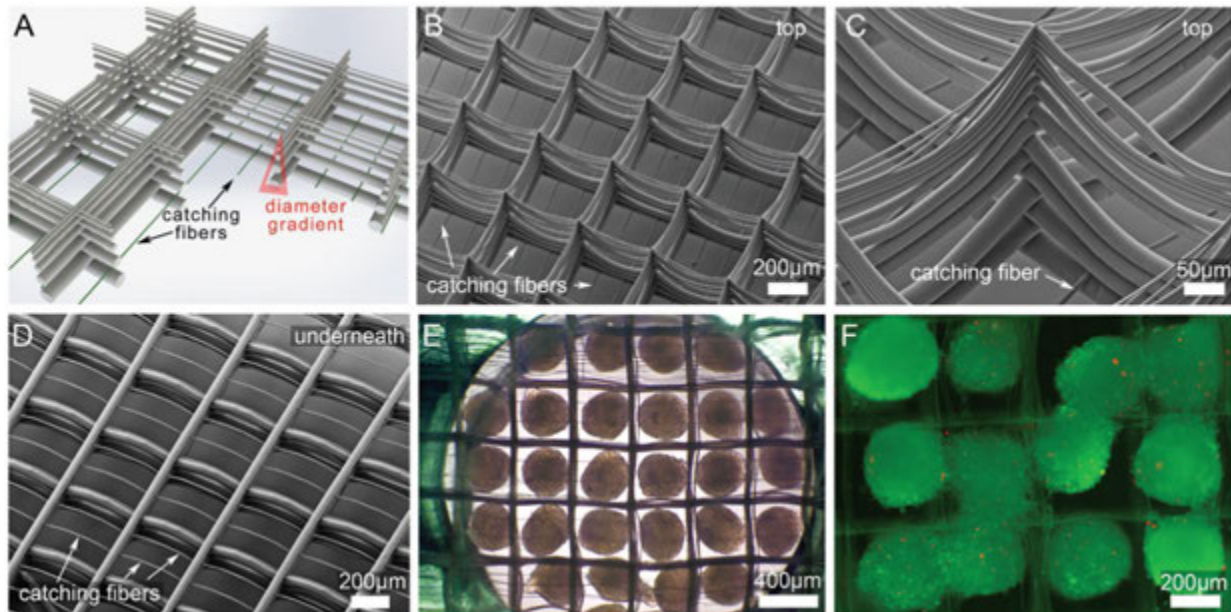


Fig. 3 Example of 3D printed PCL scaffold using MEW. Melt electrospun mesh of PCL starting with large diameter fibers (40 μm) at the bottom, down in diameter to 4 μm at the highest point. Included two 7.5 μm diameter “catching fibers” between the two large diameter fibers. (A) Schematic of tapered scaffold, (B)–(D) SEM micrographs from both sides of scaffolds, (E) 3D spheroids generated from 5000 human adipose-derived stem cells (hASCs) each in agarose-coated 96-well plates, (F) Cell viability in fluorescence microscopic image. At the culture of hASC spheroids, catching fibers inhibit spheroids from falling through the scaffold. Adapted from Hrynevich, A., Elçi, B.Ş., Haigh, J.N., *et al.*, 2018. Dimension-based design of melt electrospun scaffolds. *Small* 14 (22), 1800232.

full-thickness skin wounds, can be difficult to repair. Bioengineered skin scaffolds can be fabricated from both natural and synthetic materials and cellularized in vitro. Most recently, a patient-specific 3D printed mask for facial skin reconstruction; an engineered skin substitute combining a wound dressing layer that fits onto the facial wounds has been reported (Seol *et al.*, 2018). The product printed, *BioMask* (not to be confused with the trademarked antimicrobial face mask of the same name); consisted of three layers; a porous polyurethane (PU) layer, a keratinocyte-laden hydrogel layer, and a fibroblast-laden hydrogel layer improved regeneration of skin tissue, consisting of epidermis and dermis layers, on the complex facial wounds in a mouse model (Seol *et al.*, 2018).

The printability of 3D structures containing cells and ECM components has progressed to simplified biological tissues, however, bioprinting of functional organs remains a challenge (Daly *et al.*, 2016b). An alternative approach to directly bioprinting complex solid organs is to bioprint their less complex developmental precursors using tissue-specific stem cells. Multiple-tool biofabrication (reinforcement of stem cell laden hydrogel constructs by parallel deposition of a thermoplastic polymer fiber) has been used to engineer anatomically accurate, hypertrophic cartilage templates with the capacity to mature over time in vivo into vascularized bone organs (Daly *et al.*, 2016b). These bioprinted precursors matched the overall shape of the bone organ (Daly *et al.*, 2016b), potentially enabling their use for complex clinical applications.

A major challenge for manufacturing functional tissue is the ability to replicate highly vascularized tissues containing entangled networks of blood vessels such the pulmonary, liver, and urinary systems possessing hollow and tubular structures. Extrudable liver-specific bioinks of HA and gelatin-based hydrogels with primary liver spheroids have been used to construct in vitro liver structures with suitable stiffnesses and high cell viability (Skardal *et al.*, 2015). iPSC-derived hepatic spheroids within alginate/Pluronic F-127 bioinks together with iPSC-derived non-parenchymal cells, have also been developed as autologous liver grafts (Goulart *et al.*, 2019). Hydrogels combined with patient derived cells have been used to print thick and vascularized cardiac patches designed to match the anatomical structure of the left ventricle (Noor *et al.*, 2019). Moreover, this same study demonstrated printability of volumetric structure of small-scale cellularized human heart (height: 20 mm; diameter: 14 mm) within the support medium of two discrete bioinks, containing Cy5-prestained CMs or RFP-expressing ECs (Noor *et al.*, 2019).

Polymer-Based Biomaterials for Extrusion Techniques

The ultimate aim of 3D biofabrication approaches is to engineer biocompatible tissue structures with precise architectures and mechanical strength. A key influence on this aim is the selection of the materials to form the desired shape. Therefore, the chemical, rheological, mechanical and biological properties of the printable bioink must be considered. Extrusion printers are employed to process the bioink which themselves are affected by mechanical forces and shear stresses during the deposition from the nozzle. Bioinks with viscoelastic behavior, such as shear thinning characteristics, are promising candidates to compensate for this high shear stress associated due to their high viscosity (Guvendiren, 2019). The extrusion process typically uses a pneumatic actuator or screw device to feed natural or synthetic material through a nozzle or needle to lay in layer-by-layer fashion and forms a digital 3D object (Placone and Engler, 2018). Scaffolds with complex geometries require carefully chosen materials which match the printing conditions for specific applications. The major criteria include biodegradability, pore interconnectivity, pore size, porosity, mechanical and physical properties that are essential for the target tissue that needs to be engineered such as bone, cartilage, blood vessel, or skin.

Some of the popular biopolymers for the extrusion methods are Acrylonitrile Butadiene Styrene (ABS), Polycarbonates (PC), Polyphenylsulfone (PPSU), nylon, Polyether ether ketone (PEEK), Polyetherimide (PEI: also known as ULTEM), thermoplastic Polyurethane (PU), aliphatic polyesters such as PCL, PLA and poly glycolic acid (PGA) and natural/synthetic hydrogels (Dhinakaran *et al.*, 2020; Gregor *et al.*, 2017; Zhao *et al.*, 2018).

Thermoplastic Materials

Biodegradable polymeric materials in both natural and synthetic categories are favored to promote the organization, growth, and differentiation of cells in 3D structures (Gregor *et al.*, 2017). PCL is often used in Food and Drug Administration (FDA) approved devices and implants, and possessing a low melting point ($\sim 60^{\circ}\text{C}$) and a compressive modulus in the range of 300 MPa (Eshraghi and Das, 2010); is commonly used to produce scaffolds for both load bearing and non-load bearing applications (Siddiqui *et al.*, 2018). Polymer blends with bio-ceramics such as hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP) and biphasic calcium phosphate (BCP) offer osteoinductive and osteoconductive properties (Huang *et al.*, 2018). PLA is a biodegradable polymer commonly used for orthopedic and dental applications, for example as screws, pins and arrows in surgeries including the items of the mandibular joint, facelifts, bone fragments, meniscus repair, hyaline cartilage fixation, and ligament reconstructions (Narayanan *et al.*, 2016). FDM fabricated PCL-HA porous scaffolds can meet the bone repair requirements in terms of mechanical strength, providing a potential alternative to autografts and allograft for bone regeneration (Yao *et al.*, 2015).

To date, PCL (Brown *et al.*, 2016), Poly(propylene) (PP) (Nayak *et al.*, 2012), Poly(2-ethyl-2-oxazoline) (POZ) (Hochleitner *et al.*, 2014), Poly-Hydroxymethyl glycolide-*co*- ϵ -caprolactone (pHMGCL) (Castilho *et al.*, 2017), PEG-block-PCL (Dalton *et al.*, 2008), PLGA (Kim *et al.*, 2010), PLA (Zhou *et al.*, 2006), PMMA (Wang and Huang, 2009), poly(urea-siloxane) (Hochleitner *et al.*, 2018) and poly(L-lactide-*co*- ϵ -caprolactone-*co*-acryloyl carbonate) (Chen *et al.*, 2016) have been reported to be printable with MEW.

Melt-electrowritten constructs of pHMGCL with a rectangular pattern yielded a directional mechanical anisotropy in scaffolds enabling alignment of cardiac progenitor preferentially along the dominating direction of the scaffold fibers (Castilho *et al.*, 2017).

Other reported designs detail development of a cell-free electroconductive melt-electrowritten PCL patch with an auxetic missing-rib design which conforms to the mechanics of human myocardium (Olvera *et al.*, 2020). This same study described functionalization using polypyrrole to yield conductivity in the range of 2–2.5 S m⁻¹ and cytocompatibility with human mesenchymal stromal cells.

Despite the ease of processing and biocompatibility of many thermoplastic polymers, a significant drop in elastic modulus can occur due to plasticizing effect of absorbed water (Surrao *et al.*, 2012) and elongation caused by creep (Chen *et al.*, 2014) in environments where materials are subjected to dynamic loading (Chen *et al.*, 2016). It is believed that crosslinking of polymer chains not only improves the stiffness and creep resistance, but also reduces this plasticizing effect (Landel and Nielsen, 1993).

As a result, using a cross-linkable polymer during MEW can facilitate a high modulus upon hydration (Chen *et al.*, 2016). This has led to reports of photo-cross-linked fiber scaffolds synthesized from ϵ -caprolactone (ϵ -CL), L-lactide (LLA), and a trimethylene carbonate-based monomer carry an acryloyl pendant group (5-methyl-2-oxo-1,3-dioxan-5-yl acrylate, or acryloyl carbonate (AC)), used to achieve an average modulus of 26 MPa in post-hydration conditions (Chen *et al.*, 2014).

Hydrogels

Extrusion-based technologies can utilize a wide range of materials presented in the liquid state (or materials that sufficiently shear thin during extrusion) that can then quickly solidify (Gibson *et al.*, 2014). Hydrogels with 3D viscoelastic polymeric structures display physical properties comparable with natural tissue which can be harnessed to match the final application in regenerative medicine (Lee and Kim, 2018). These materials are particularly suitable for use as bioinks harboring cells during the printing process; however there exists a defined range of opportunity, often termed the 'biofabrication window'; a concept that dictates the compromises between the printability of a bioink formulation and maintaining appropriate cell viability (Levato *et al.*, 2020). Printability will be dictated by bioink rheological properties and stiffness which will have a direct influence on shear stress, mechanosensing and nutrient perfusion experienced by embedded cells. Naturally derived hydrogels can be categorized in three groups as protein-based, polysaccharide-based and those derived from decellularized tissue (Catoira *et al.*, 2019). Collagen, elastin, fibrin, gelatin as protein-based natural hydrogels and polysaccharide-based materials such as agarose, alginate and chitosan (Catoira *et al.*, 2019) are precursors which can be extruded in a jelly-like form and then crosslinked with UV, ion or temperature-assisted during the post processing step (Wang *et al.*, 2020). A limitation of hydrogels is poor mechanical properties leading to eliminate their application in high load bearing situations (Daly *et al.*, 2016a). Therefore, constructs aiming to withstand such situations require reinforcement non-hydrogel inks.

Natural protein hydrogel bioinks

Collagen as the main insoluble fibrous protein in the body has long been used in tissue engineered scaffolds (Catoira *et al.*, 2019). 3D bioprinted constructs of collagen type I (COL) with sodium alginate (SA) and chondrocytes have been reported to possess favorable mechanical strength and biological functionality (Yang *et al.*, 2018b). In other work, a highly porous construct of cell-laden collagen/polyphenol was fabricated using a 3D cell printing system (Yeo and Kim, 2017). This hybrid structure, consisting of core-shell struts laden with hASCs and single struts with preosteoblasts (MC3T3-E1), exhibited improved cellular viability when compared to a standard alginate control ink (Yeo and Kim, 2017). Fibrin, a protein found in circulating blood; has been adapted to hydrogels that support stem cell culture and differentiation (Abelseth *et al.*, 2019). One biofabrication approach in the tissue engineering of a urethra has explored the construction of porous PCL/PLCL scaffolds within fibrin hydrogels. The resultant spiral scaffold contained multiple layers harboring urothelial cells and smooth muscle cells and possessed mechanical properties equal to the native urethra in rabbits (Zhang *et al.*, 2017). The high level of porosity in the scaffold facilitated cell-cell interaction between cell layers and a uniform nutrient transport inside the scaffold (Zhang *et al.*, 2017).

Polysaccharide-based hydrogel bioinks

Hyaluronic acid (HA) is a polysaccharide-based material and a major component of the extracellular matrix extensively found in vitreous and synovial fluids (Yoo *et al.*, 2005). HA has a slow gelation rate with low mechanical properties which is a major barrier to its use for scaffold generation (Noh, 2018). However, HA can be combined with natural/synthetic polymers to modify and meet the mechanical requirements for different applications such as cartilage tissue. A tailor-made methacrylated hyaluronic acid (MeHA) gel has been reported for the development of 3D printable scaffolds supporting bone-like tissue formation showing high levels of cell survival and spontaneous osteogenic differentiation in vitro (Poldervaart *et al.*, 2017).

Agarose is a thermo reversible polymer, suitable for diverse applications because of its reliable and robust gel forming properties (Xiong *et al.*, 2005). Hydrogel blends of agarose have been shown to yield stable 3D constructs and support endothelial and fibroblast cell growth (Kreimendahl *et al.*, 2017). Alginate as a biopolymer are negatively charged polysaccharides, can entrap water and other molecules via capillary forces and allow diffusion from inside out. This distinctive property makes it an attractive candidate for 3D printing bioinks (Gopinathan and Noh, 2018b). High strength 3D structures of cell-laden alginate-based hydrogel have been fabricated with fusion of adjacent hollow filaments (Gao *et al.*, 2015). The hollow alginate filaments support the mechanical integrity of the 3D bioprinting structure and work as built-in microchannels to deliver nutrients for cell growth (Gao *et al.*, 2015). In another study, a printability window for different molecular weights of alginate by varying the ratio of alginate to ionic crosslinker has been described and used to spatially define microenvironments and cellular phenotypes found in solid organs like a long bone using 3D bioprinting (Freeman and Kelly, 2017).

Synthetic and interpenetrating network hydrogel bioinks

Synthetic hydrogels possess the benefits such as precise control, reproducibility and desired mechanical properties with low toxicity which make them suitable candidates for cell-laden and drug carrying inks (Zhao *et al.*, 2018). Classic synthetic polymers employed in tissue engineering hydrogel scaffolds are synthetic PEG, Polyvinyl alcohol (PVA), Polyacrylamide (PAM) and Pluronic (Gopinathan and Noh, 2018b; Meng *et al.*, 2020). The most commonly used PEG-based bioinks in extrusion-based technique (Cui *et al.*, 2012; Wüst *et al.*, 2015) are PEGDA and poly(ethylene glycol) methacrylate (PEGMA) to improve the mechanical properties of 3D constructs. On-board photo-crosslinking systems have been used to enable 3D extrusion and curing of PEGDA hydrogels to achieve complex aortic valve geometries (Hockaday *et al.*, 2012). This work demonstrates that hydrogel extrusion is able to fabricate anatomical heterogeneous valve conduits which support cell engraftment (Hockaday *et al.*, 2012). PVA-based composite hydrogels proposed as part of an artificial cartilage replacement with a biomimetic gradient structure prepared via micro extrusion technology exhibited attractive bio-mechanical and bio-friction properties (Meng *et al.*, 2020).

Synthetic hydrogels with controlled mechanical and chemical properties, such as gelatin methacryloyl (GelMA) and PEGDA have been used as bioinks and cross-linked via click chemistry (Gopinathan and Noh, 2018a), ionic or physical bonding, thermo gelation, enzyme-enabled crosslinking and photopolymerization (Li *et al.*, 2018).

HA, hydroxyethyl acrylate (HEA) and gelatin-methacryloyl (HA-g-pHEA-gelatin) hydrogel based bioinks have demonstrated stable rheological properties and biocompatibility when printed in lattice forms (Noh *et al.*, 2019). A double network hydrogel with superior shear-thinning and recovery properties of gellan gum (GG) and fast UV cross-linking capability of PEGDA has been reported used as an encapsulating bioink for BMSCs and mouse osteoblastic cells encapsulated to create constructs modeling the ear and nose with high fidelity. This platform demonstrated biocompatibility and promise for the fabrication of living tissues at a human scale (Wu *et al.*, 2018).

Present approaches of the extrusion-based bioprinting have obtained significant advances but require considerable improvement. For instance, microstructure and anisotropy control in cell-seeded structures at a low cost while ensuring high quality is still a challenge in 3D printing. A move to 3D-bioprinting of collagen via freeform reversible embedding of suspended hydrogels (FRESH) to engineer functional organs has emerged in recent times (Lee *et al.*, 2019). FRESH operates by extruding a liquid from a syringe into a slurry, where the extruded material self-assembles into a solid filament (Hinton *et al.*, 2015). Recently, FRESH-printing of a left ventricle cardiac model using human stem cell-derived cardiomyocytes has been reported whereby a dual-material printing of a structural collagen bioink in combination with a high density cell bioink (Lee *et al.*, 2019). A neonatal scale human heart was fabricated using collagen which detailed the internal structure via printing of a cross-sectional view of (Lee *et al.*, 2019).

Conclusion

In summary, AM innovations in material design and fabrication processes could open up new developments in healthcare. The ability to use different 3D printing approaches with a large variety of polymers and their blends is still an emerging field. To achieve the optimal bioink, vascularization, compatibility and cell proliferation are fundamental factors to support tissue function in porous structures. Thus far, the field of additive manufacturing, specifically 3D printing in healthcare seeks to develop ideal polymeric materials to print engineering tissue constructions for mimicking biological entities and stimulating cell response which cause tissue regeneration and repair.

This article demonstrates the potential of extrusion-based technique for engineering personalized tissues and recapitulating patient-specific biochemical and biophysical microenvironments. However, despite recent improvements in design, inspired structures, and bioactivity of new polymeric materials to mimic native tissue, future research must address current limitations such as resolution, scalability, and the repertoire of materials available for these processes.

References

- Abelseth, E., Abelseth, L., De la Vega, L., *et al.*, 2019. 3D printing of neural tissues derived from human induced pluripotent stem cells using a fibrin-based bioink. *ACS Biomaterials Science & Engineering* 5 (1), 234–243.
- Afghah, F., Dikyol, C., Altunbek, M., Koc, B., 2019. Biomimicry in bio-manufacturing: developments in melt electrospinning writing technology towards hybrid biomanufacturing. *Applied Sciences* 9 (17), 3540.
- Allied Market Research, 2019. 3D printing healthcare market. Available at: <https://www.alliedmarketresearch.com/3d-printing-healthcare-market>.
- Azad, M.A., Olawuni, D., Kimbell, G., *et al.*, 2020. Polymers for extrusion-based 3D printing of pharmaceuticals: A holistic materials–process perspective. *Pharmaceutics* 12 (2), 124.
- Baldwin, J., Wagner, F., Martine, L., *et al.*, 2017. Periosteum tissue engineering in an orthotopic in vivo platform. *Biomaterials* 121, 193–204.
- Bas, O., De-Juan-Pardo, E.M., Meinert, C., *et al.*, 2017. Biofabricated soft network composites for cartilage tissue engineering. *Biofabrication* 9 (2), 025014.
- Bas, O., Lucarotti, S., Angella, D.D., *et al.*, 2018. Rational design and fabrication of multiphasic soft network composites for tissue engineering articular cartilage: A numerical model-based approach. *Chemical Engineering Journal* 340, 15–23.
- Bendtsen, S.T., Quinnell, S.P., Wei, M., 2017. Development of a novel alginate-polyvinyl alcohol-hydroxyapatite hydrogel for 3D bioprinting bone tissue engineered scaffolds. *Journal of Biomedical Materials Research Part A* 105 (5), 1457–1468.
- Biglino, G., Verschueren, P., Zegels, R., Taylor, A.M., Schievano, S., 2013. Rapid prototyping compliant arterial phantoms for in-vitro studies and device testing. *Journal of Cardiovascular Magnetic Resonance* 15 (1), 2.
- Bose, S., Ke, D., Sahasrabudhe, H., Bandyopadhyay, A., 2018. Additive manufacturing of biomaterials. *Progress in Materials Science* 93, 45–111.
- Bose, S., Vahabzadeh, S., Bandyopadhyay, A., 2013. Bone tissue engineering using 3D printing. *Materials Today* 16 (12), 496–504.

- Brown, T.D., Dalton, P.D., Hutmacher, D.W., 2016. Melt electrospinning today: An opportune time for an emerging polymer process. *Progress in Polymer Science* 56, 116–166.
- Brown, T.D., Sliotsoch, A., Thibaut, L., *et al.*, 2012. Design and fabrication of tubular scaffolds via direct writing in a melt electrospinning mode. *Biointerphases* 7 (1), 13.
- Buj-Corral, I., Bagheri, A., Petit-Rojo, O., 2018. 3D printing of porous scaffolds with controlled porosity and pore size values. *Materials* 11 (9), 1532.
- Cardwell, R.D., Dahlgren, L.A., Goldstein, A.S., 2014. Electrospun fibre diameter, not alignment, affects mesenchymal stem cell differentiation into the tendon/ligament lineage. *Journal of Tissue Engineering and Regenerative Medicine* 8 (12), 937–945.
- Castilho, M., Feyen, D., Flandes-Iparraguirre, M., *et al.*, 2017. Melt electrospinning writing of poly-hydroxymethylglycolide-co- ϵ -caprolactone-based scaffolds for cardiac tissue engineering. *Advanced Healthcare Materials* 6 (18), 1700311.
- Catoira, M.C., Fusaro, L., Di Francesco, D., Ramella, M., Boccafroschi, F., 2019. Overview of natural hydrogels for regenerative medicine applications. *Journal of Materials Science: Materials in Medicine* 30 (10), 115.
- Chang, R., Nam, J., Sun, W., 2008. Effects of dispensing pressure and nozzle diameter on cell survival from solid freeform fabrication-based direct cell writing. *Tissue Engineering Part A* 14 (1), 41–48.
- Chen, F., Hayami, J.W.S., Amsden, B.G., 2014. Electrospun poly(l-lactide-co-acryloyl carbonate) fiber scaffolds with a mechanically stable crimp structure for ligament tissue engineering. *Biomacromolecules* 15 (5), 1593–1601.
- Chen, F., Hochleitner, G., Woodfield, T., *et al.*, 2016. Additive manufacturing of a photo-cross-linkable polymer via direct melt electrospinning writing for producing high strength structures. *Biomacromolecules* 17 (1), 208–214.
- Crump, S.S., 1992. Apparatus and method for creating three-dimensional objects. U.S. Patent 5,121,329. Google Patent.
- Cui, X., Breitenkamp, K., Finn, M., Lotz, M., D'Lima, D.D., 2012. Direct human cartilage repair using three-dimensional bioprinting technology. *Tissue Engineering Part A* 18 (11–12), 1304–1312.
- Dalton, P.D., Grafahrend, D., Klinkhammer, K., Klee, D., Möller, M., 2007. Electrospinning of polymer melts: Phenomenological observations. *Polymer* 48 (23), 6823–6833.
- Dalton, P.D., Joergensen, N.T., Groll, J., Moeller, M., 2008. Patterned melt electrospun substrates for tissue engineering. *Biomedical Materials* 3 (3), 034109.
- Dalton, P.D., Lleixà Calvet, J., Mourran, A., Klee, D., Möller, M., 2006. Melt electrospinning of poly-(ethylene glycol-block- ϵ -caprolactone). *Biotechnology Journal: Healthcare Nutrition Technology* 1 (9), 998–1006.
- Dalton, P.D., Vaquette, C., Farrugia, B.L., *et al.*, 2013. Electrospinning and additive manufacturing: Converging technologies. *Biomaterials Science* 1 (2), 171–185.
- Daly, A.C., Critchley, S.E., Rencsok, E.M., Kelly, D.J., 2016a. A comparison of different bioinks for 3D bioprinting of fibrocartilage and hyaline cartilage. *Biofabrication* 8 (4), 045002.
- Daly, A.C., Cuniffe, G.M., Sathy, B.N., *et al.*, 2016b. 3D bioprinting of developmentally inspired templates for whole bone organ engineering. *Advanced Healthcare Materials* 5 (18), 2353–2362.
- Derakhshanfar, S., Mbeleck, R., Xu, K., *et al.*, 2018. 3D bioprinting for biomedical devices and tissue engineering: A review of recent trends and advances. *Bioactive Materials* 3 (2), 144–156.
- Dhinakaran, V., Manoj Kumar, K.P., Bupathi Ram, P.M., Ravichandran, M., Vinayagamoorthy, M., 2020. A review on recent advancements in fused deposition modeling. *Materials Today: Proceedings*.
- Duan, B., Hockaday, L.A., Kang, K.H., Butcher, J.T., 2013. 3D bioprinting of heterogeneous aortic valve conduits with alginate/gelatin hydrogels. *Journal of Biomedical Materials Research Part A* 101 (5), 1255–1264.
- Eichholz, K.F., Hoey, D.A., 2018. Mediating human stem cell behaviour via defined fibrous architectures by melt electrospinning writing. *Acta Biomaterialia* 75, 140–151.
- Eshraghi, S., Das, S., 2010. Mechanical and microstructural properties of polycaprolactone scaffolds with one-dimensional, two-dimensional, and three-dimensional orthogonally oriented porous architectures produced by selective laser sintering. *Acta Biomater* 6 (7), 2467–2476.
- Farrugia, B.L., Brown, T.D., Upton, Z., *et al.*, 2013. Dermal fibroblast infiltration of poly (ϵ -caprolactone) scaffolds fabricated by melt electrospinning in a direct writing mode. *Biofabrication* 5 (2), 025001.
- Freeman, F.E., Kelly, D.J., 2017. Tuning alginate bioink stiffness and composition for controlled growth factor delivery and to spatially direct msc fate within bioprinted tissues. *Scientific Reports* 7 (1), 17042.
- Fuchs, R.K., Thompson, W.R., Warden, S.J., 2019. Chapter 2 – Bone biology. In: Pawelec, K.M., Planell, J.A. (Eds.), *Bone Repair Biomaterials*, second ed. Woodhead Publishing, pp. 15–52.
- Future Market Insights, F., 2019. 3D printed medical devices market-2019–2029.
- Gao, Q., He, Y., Fu, J.-z., Liu, A., Ma, L., 2015. Coaxial nozzle-assisted 3D bioprinting with built-in microchannels for nutrients delivery. *Biomaterials* 61, 203–215.
- Garzon-Hernandez, S., Garcia-Gonzalez, D., Jérusalem, A., Arias, A., 2020. Design of FDM 3D printed polymers: An experimental-modelling methodology for the prediction of mechanical properties. *Materials & Design* 188, 108414.
- Gibson, I., Rosen, D., Stucker, B., 2014a. *Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing*. New York: Springer.
- Goodridge, R., Ziegemeier, S., 2017. Chapter 7 – Powder bed fusion of polymers. In: Brandt, M. (Ed.), *Laser Additive Manufacturing*. Woodhead Publishing, pp. 181–204.
- Gopinathan, J., Noh, I., 2018a. Click chemistry-based injectable hydrogels and bioprinting inks for tissue engineering applications. *Tissue Engineering and Regenerative Medicine* 15 (5), 531–546.
- Gopinathan, J., Noh, I., 2018b. Recent trends in bioinks for 3D printing. *Biomaterials Research* 22, 11. [11].
- Goulart, E., de Caires-Junior, L.C., Telles-Silva, K.A., *et al.*, 2019. 3D bioprinting of liver spheroids derived from human induced pluripotent stem cells sustain liver function and viability in vitro. *Biofabrication* 12 (1), 015010.
- Gregor, A., Filová, E., Novák, M., *et al.*, 2017. Designing of PLA scaffolds for bone tissue replacement fabricated by ordinary commercial 3D printer. *Journal of Biological Engineering* 11, 31.
- Grottkau, B.E., Hui, Z., Yao, Y., Pang, Y., 2020. Rapid fabrication of anatomically-shaped bone scaffolds using indirect 3d printing and perfusion techniques. *International Journal of Molecular Sciences* 21 (1), 315.
- Guvendiren, M., 2019. *3D Bioprinting in Medicine: Technologies, Bioinks, and Applications*. Springer International Publishing.
- Haigh, J.N., Chuang, Y.-m., Farrugia, B., *et al.*, 2016. Hierarchically structured porous poly(2-oxazoline) hydrogels. *Macromolecular Rapid Communications* 37 (1), 93–99.
- Han, X., Yang, D., Yang, C., *et al.*, 2019. Carbon fiber reinforced peek composites based on 3D-printing technology for orthopedic and dental applications. *Journal of Clinical Medicine* 8 (2), 240.
- Healthcare IT News, 2020. Volunteers use 3D-printing to support Italian COVID-19 effort.
- Hinton, T.J., Jallierat, Q., Palchesko, R.N., *et al.*, 2015. Three-dimensional printing of complex biological structures by freeform reversible embedding of suspended hydrogels. *Science Advances* 1 (9), e1500758.
- Hochleitner, G., Fursattel, E., Giesa, R., *et al.*, 2018. Melt electrowriting of thermoplastic elastomers. *Macromolecular Rapid Communications* 39 (10), e1800055.
- Hochleitner, G., Hümmer, J.F., Luxenhofer, R., Groll, J., 2014. High definition fibrous poly (2-ethyl-2-oxazoline) scaffolds through melt electrospinning writing. *Polymer* 55 (20), 5017–5023.
- Hochleitner, G., Youssef, A., Hrynevich, A., *et al.*, 2016. Fibre pulsing during melt electrospinning writing. *BioNanoMaterials* 17 (3–4), 159.
- Hockaday, L.A., Kang, K.H., Colangelo, N.W., *et al.*, 2012. Rapid 3D printing of anatomically accurate and mechanically heterogeneous aortic valve hydrogel scaffolds. *Biofabrication* 4 (3), 035005.
- Hrynevich, A., Elçi, B.S., Haigh, J.N., *et al.*, 2018. Dimension-based design of melt electrowritten scaffolds. *Small* 14 (22), 1800232.
- Huang, B., Caetano, G., Vyas, C., *et al.*, 2018. Polymer-ceramic composite scaffolds: The effect of hydroxyapatite and β -tri-calcium phosphate. *Materials* 11 (1), 129.

- Hutmacher, D.W., 2001. Scaffold design and fabrication technologies for engineering tissues – State of the art and future perspectives. *Journal of Biomaterials Science, Polymer Edition* 12 (1), 107–124.
- Jariwala, S.H., Lewis, G.S., Bushman, Z.J., Adair, J.H., Donahue, H.J., 2015. 3D printing of personalized artificial bone scaffolds. *3D Printing and Additive Manufacturing* 2 (2), 56–64.
- Jungst, T., Muerza-Cascante, M.L., Brown, T.D., *et al.*, 2015. Melt electrospinning onto cylinders: Effects of rotational velocity and collector diameter on morphology of tubular structures. *Polymer International* 64 (9), 1086–1095.
- Kelly, C.N., Miller, A.T., Hollister, S.J., Guldberg, R.E., Gall, K., 2018. Design and structure-function characterization of 3D printed synthetic porous biomaterials for tissue engineering. *Advanced Healthcare Materials* 7 (7), 1701095.
- Kempin, W., Franz, C., Koster, L.-C., *et al.*, 2017. Assessment of different polymers and drug loads for fused deposition modeling of drug loaded implants. *European Journal of Pharmaceutics and Biopharmaceutics* 115, 84–93.
- Kim, S.J., Park, W.H., Min, B.-M., 2010. Fabrication and characterization of 3-dimensional PLGA nanofiber/microfiber composite scaffolds. *Polymer* 51 (6), 1320–1327.
- Kreimendahl, F., Köpf, M., Thiebes, A.L., *et al.*, 2017. Three-dimensional printing and angiogenesis: Tailored agarose-type I collagen blends comprise three-dimensional printability and angiogenesis potential for tissue-engineered substitutes. *Tissue Engineering Part C: Methods* 23 (10), 604–615.
- Lam, R.H.W., Chen, W., 2019. *Biomedical Devices: Materials, Design, and Manufacturing*. Springer International Publishing.
- Landel, R.F., Nielsen, L.E., 1993. *Mechanical Properties of Polymers and Composites*. CRC press.
- Lee, A., Hudson, A.R., Shiwarski, D.J., *et al.*, 2019. 3D bioprinting of collagen to rebuild components of the human heart. *Science* 365 (6452), 482–487.
- Lee, J.-H., Kim, H.-W., 2018. Emerging properties of hydrogels in tissue engineering. *Journal of Tissue Engineering* 9. 2041731418768285.
- Levato, R., Jungst, T., Scheuring, R.G., *et al.*, 2020. From shape to function: The next step in bioprinting. *Advanced Materials* 32 (12), 1906423.
- Li, J., Li, L., Zhou, J., *et al.*, 2019. 3D printed dual-functional biomaterial with self-assembly micro-nano surface and enriched nano argentum for antibacterial and bone regeneration. *Applied Materials Today* 17, 206–215.
- Li, X., Sun, Q., Li, Q., Kawazoe, N., Chen, G., 2018. Functional hydrogels with tunable structures and properties for tissue engineering applications. *Frontiers in chemistry* 6, 499. [499].
- Lim, S.H., Kathuria, H., Tan, J.J.Y., Kang, L., 2018. 3D printed drug delivery and testing systems – A passing fad or the future? *Advanced Drug Delivery Reviews* 132, 139–168.
- Markets and Markets™, 2017. 3D printing medical devices market by technology – Global forecast to 2022.
- Materialise, 2020. Materialise develops 3D printed oxygen peep mask to address shortage of ventilators.
- Meng, Y., Cao, J., Chen, Y., Yu, Y., Ye, L., 2020. 3D printing of a poly(vinyl alcohol)-based nano-composite hydrogel as an artificial cartilage replacement and the improvement mechanism of printing accuracy. *Journal of Materials Chemistry B* 8 (4), 677–690.
- Mertz, L., 2013. Dream it, design it, print it in 3-D: What can 3-D printing do for you? *IEEE Pulse* 4 (6), 15–21.
- Murphy, S.V., Atala, A., 2014. 3D bioprinting of tissues and organs. *Nature Biotechnology* 32 (8), 773–785.
- Musarrat, H.W., Mohammad, Y., Majed Al, R., *et al.*, 2018. 3D printing methods for pharmaceutical manufacturing: Opportunity and challenges. *Current Pharmaceutical Design* 24 (42), 4949–4956.
- Narayanan, G., Vernekar, V.N., Kuyinu, E.L., Laurencin, C.T., 2016. Poly (lactic acid)-based biomaterials for orthopaedic regenerative engineering. *Advanced Drug Delivery Reviews* 107, 247–276.
- Nayak, R., Kyratzis, I.L., Truong, Y.B., Padhye, R., Arnold, L., 2012. Melt-electrospinning of polypropylene with conductive additives. *Journal of Materials Science* 47 (17), 6387–6396.
- Noh, I., 2018. *Biomimetic Medical Materials: From Nanotechnology to 3D Bioprinting*. Singapore: Springer.
- Noh, I., Kim, N., Tran, H.N., Lee, J., Lee, C., 2019. 3D printable hyaluronic acid-based hydrogel for its potential application as a bioink in tissue engineering. *Biomaterials Research* 23, 3.
- Noor, N., Shapira, A., Edri, R., *et al.*, 2019. 3D printing of personalized thick and perfusable cardiac patches and hearts. *Advanced Science* 6 (11), 1900344.
- Norman, J., Madurawe, R.D., Moore, C.M., Khan, M.A., Khairuzzaman, A., 2017. A new chapter in pharmaceutical manufacturing: 3D-printed drug products. *Advanced Drug Delivery Reviews* 108, 39–50.
- Nyberg, E., Rindone, A., Dorafshar, A., Grayson, W.L., 2016. Comparison of 3D-printed poly-ε-caprolactone scaffolds functionalized with tricalcium phosphate, hydroxyapatite, bio-oss, or decellularized bone matrix. *Tissue Engineering Part A* 23 (11–12), 503–514.
- Olvera, D., Sohrabi Molina, M., Hendy, G., Monaghan, M.G., 2020. Electroconductive melt electrowritten patches matching the mechanical anisotropy of human myocardium. *Advanced Functional Materials* 30, 1909880.
- Petcu, E.B., Midha, R., McColi, E., *et al.*, 2018. 3d printing strategies for peripheral nerve regeneration. *Biofabrication* 10 (3), 032001.
- Placone, J.K., Engler, A.J., 2018. Recent advances in extrusion-based 3D printing for biomedical applications. *Advanced Healthcare Materials* 7 (8), 1701161.
- Poldervaart, M.T., Goversen, B., de Ruijter, M., *et al.*, 2017. 3D bioprinting of methacrylated hyaluronic acid (meHA) hydrogel with intrinsic osteogenicity. *PLoS one* 12 (6), e0177628. [e0177628].
- Richbourg, N.R., Peppas, N.A., Sikavitsas, V.I., 2019. Tuning the biomimetic behavior of scaffolds for regenerative medicine through surface modifications. *Journal of Tissue Engineering and Regenerative Medicine* 13 (8), 1275–1293.
- Rider, P., Kačarević, Ž.P., Alkildani, S., Retnasingh, S., Barbeck, M., 2018. Bioprinting of tissue engineering scaffolds. *Journal of Tissue Engineering* 9. [2041731418802090].
- Robinson, T.M., Hutmacher, D.W., Dalton, P.D., 2019. The next frontier in melt electrospinning: Taming the jet. *Advanced Functional Materials* 29 (44), 1904664.
- Safari, A., Danforth, S.C., Allahverdi, M., Venkataraman, N., 2001. Rapid prototyping. In: Buschow, K.H.J., Cahn, R.W., Flemings, M.C., *et al.* (Eds.), *Encyclopedia of Materials: Science and Technology*. Oxford: Elsevier, pp. 7991–8003.
- Senatov, F.S., Niaza, K.V., Zadorozhnyy, M.Y., *et al.*, 2016. Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds. *Journal of the Mechanical Behavior of Biomedical Materials* 57, 139–148.
- Seol, Y.-J., Lee, H., Copus, J.S., *et al.*, 2018. 3D bioprinted biomask for facial skin reconstruction. *Bioprinting* 10, e00028.
- Shin, H., Jo, S., Mikos, A.G., 2003. Biomimetic materials for tissue engineering. *Biomaterials* 24 (24), 4353–4364.
- Siddiqui, N., Asawa, S., Birru, B., Baadhe, R., Rao, S., 2018. PCL-based composite scaffold matrices for tissue engineering applications. *Mol Biotechnol* 60 (7), 506–532.
- Skardal, A., Devarasetty, M., Kang, H.-W., *et al.*, 2015. A hydrogel bioink toolkit for mimicking native tissue biochemical and mechanical properties in bioprinted tissue constructs. *Acta Biomaterialia* 25, 24–34.
- Surrao, D.C., Waldman, S.D., Amsden, B.G., 2012. Biomimetic poly(lactide) based fibrous scaffolds for ligament tissue engineering. *Acta Biomaterialia* 8 (11), 3997–4006.
- Tavares, J.M.R.S., Natal, J.R.M., 2018. Computational modelling of objects represented in images. Fundamentals, methods and applications. In: *Proceedings of the International Symposium Compimage 2006*. Coimbra, Portugal: CRC Press.
- Teo, E.Y., Ong, S.-Y., Khoo Chong, M.S., *et al.*, 2011. Polycaprolactone-based fused deposition modeled mesh for delivery of antibacterial agents to infected wounds. *Biomaterials* 32 (1), 279–287.
- The Irish Times, 2020. Coronavirus: UCD researchers using 3D printing to make medical face shields.
- Visser, J., Melchels, F.P., Jeon, J.E., *et al.*, 2015. Reinforcement of hydrogels using three-dimensionally printed microfibres. *Nature Communications* 6 (1), 1–10.
- Walmsley, G.G., McArdle, A., Tevlin, R., *et al.*, 2015. Nanotechnology in bone tissue engineering. *Nanomedicine: Nanotechnology, Biology and Medicine* 11 (5), 1253–1263.
- Wang, C., Huang, W., Zhou, Y., *et al.*, 2020. 3D printing of bone tissue engineering scaffolds. *Bioactive Materials* 5 (1), 82–91.
- Wang, X.-f., Huang, Z.-M., 2009. Melt-electrospinning of pmma. *Chinese Journal of Polymer Science* 28 (1), 45.

- Weisman, J.A., Nicholson, J.C., Tappa, K., *et al.*, 2015. Antibiotic and chemotherapeutic enhanced three-dimensional printer filaments and constructs for biomedical applications. *International Journal of Nanomedicine* 10, 357–370.
- Willemsen, K., Nizak, R., Noordmans, H.J., *et al.*, 2019. Challenges in the design and regulatory approval of 3d-printed surgical implants: A two-case series. *The Lancet Digital Health* 1 (4), e163–e171.
- Wu, D., Yu, Y., Tan, J., *et al.*, 2018. 3D bioprinting of gellan gum and poly (ethylene glycol) diacrylate based hydrogels to produce human-scale constructs with high-fidelity. *Materials & Design* 160, 486–495.
- Wunner, F.M., Bas, O., Saidy, N.T., *et al.*, 2017. Melt electrospinning writing of three-dimensional poly(ϵ -caprolactone) scaffolds with controllable morphologies for tissue engineering applications. *JoVE* 130, e56289.
- Wunner, F.M., Wille, M.-L., Noonan, T.G., *et al.*, 2018. Melt electrospinning writing of highly ordered large volume scaffold architectures. *Advanced Materials* 30 (20), 1706570.
- Wüst, S., Müller, R., Hofmann, S., 2015. 3D bioprinting of complex channels – Effects of material, orientation, geometry, and cell embedding. *Journal of Biomedical Materials Research Part A* 103 (8), 2558–2570.
- Xiong, J.-Y., Narayanan, J., Liu, X.-Y., *et al.*, 2005. Topology evolution and gelation mechanism of agarose gel. *The Journal of Physical Chemistry B* 109 (12), 5638–5643.
- Xu, N., Ye, X., Wei, D., *et al.*, 2014. 3D artificial bones for bone repair prepared by computed tomography-guided fused deposition modeling for bone repair. *ACS Applied Materials & Interfaces* 6 (17), 14952–14963.
- Yang, L., Bhaduri, S., Webster, T.J., 2018a. *Biomaterials in Translational Medicine*. Elsevier Science.
- Yang, S., Leong, K.-F., Du, Z., Chua, C.-K., 2001. The design of scaffolds for use in tissue engineering. Part I. Traditional factors. *Tissue engineering* 7 (6), 679–689.
- Yang, X., Lu, Z., Wu, H., *et al.*, 2018b. Collagen-alginate as bioink for three-dimensional (3D) cell printing based cartilage tissue engineering. *Materials Science and Engineering: C* 83, 195–201.
- Yao, Q., Wei, B., Guo, Y., *et al.*, 2015. Design, construction and mechanical testing of digital 3D anatomical data-based PCL–ha bone tissue engineering scaffold. *Journal of Materials Science: Materials in Medicine* 26 (1), 51.
- Yeo, M.G., Kim, G.H., 2017. A cell-printing approach for obtaining hasc-laden scaffolds by using a collagen/polyphenol bioink. *Biofabrication* 9 (2), 025004.
- Yoo, H.S., Lee, E.A., Yoon, J.J., Park, T.G., 2005. Hyaluronic acid modified biodegradable scaffolds for cartilage tissue engineering. *Biomaterials* 26 (14), 1925–1933.
- Zadpoor, A.A., Malda, J., 2017. Additive manufacturing of biomaterials, tissues, and organs. *Annals of Biomedical Engineering* 45 (1), 1–11.
- Zein, I., Huttmacher, D.W., Tan, K.C., Teoh, S.H., 2002. Fused deposition modeling of novel scaffold architectures for tissue engineering applications. *Biomaterials* 23 (4), 1169–1185.
- Zhang, K., Fu, Q., Yoo, J., *et al.*, 2017. 3d bioprinting of urethra with PCL/PLCL blend and dual autologous cells in fibrin hydrogel: An in vitro evaluation of biomimetic mechanical property and cell growth environment. *Acta Biomaterialia* 50, 154–164.
- Zhao, F., Li, D., Jin, Z., 2018. Preliminary investigation of poly-ether-ether-ketone based on fused deposition modeling for medical applications. *Materials* 11 (2), 288.
- Zhou, H., Green, T.B., Joo, Y.L., 2006. The thermal effects on electrospinning of polylactic acid melts. *Polymer* 47 (21), 7497–7505.

Preparation and Applications of Synergically Combined Polymer Matrix Composites

Shashank T Mhaske and Arjit Gadgeel, Institute of Chemical Technology, Mumbai, India

© 2021 Elsevier Inc. All rights reserved.

Introduction

The challenging technologies of the modern world demand the development of new materials that exhibit tailor-made nature, extensive functional and mechanical properties. In accordance with which the polymer matrix composite acquires a special place in the realm of new material development and technology related to it. The polymer matrix composite attributes that structure where the matrix phase and the reinforcing phase forms a thermodynamically stable interface and express the differential nature in terms of mechanical, rheological, and morphological properties. In addition to that, both of the phases should not be soluble to each other and always express the distinctive phases at the microstructural level. Fig. 1 expresses the fundamental criteria for defining any composite as a multifunctional composite.

The multifunctional polymer composite can be defined by understanding the four fundamental points. Both of the matrix and reinforcement should pose the distinctive characteristic in the microstructure. The matrix allows the formation of the interphase by sharing the common space around the reinforcing units. Because of this, the polymer matrix holds the reinforcement and retain the ability of the composite to sustain a higher amount of stress without showing any deformation. The absence of the distinctive phase or interface in the multifunctional composite prevents the adherence of one phase with others and thus results in an inefficient polymeric composite. Similarly, the second essential characteristic of the multifunctional composite is its integration in the properties. The multifunctional composite is the synonym for the multi-purpose materials, which means that a single material can exhibit different properties when exposed to different responses or conditions. The synergic behavior of the composite supports the multifunctional nature of the composite. The synergy in the conductivity of the matrix and magnetic nature of the reinforcement allows the tuning of the rheological properties of the composite. The final criterion which defines the multifunctional nature of the polymeric composite is its stable interphase. The interphase between the matrix and reinforcement should be thermodynamically stable.

Need and Purpose of the Multifunctional Polymer Composite

Multifunctional polymeric composite shows the sequence of simultaneously switch properties. These kinds of systems improved the performance of the base resin and embedded the system with various properties. These composite materials allow the integration in the properties of the matrix and reinforcement and thus impart the enhance multiple properties in the primary structural feature of the composite. They have the potential to impart any features such as magnetic, electrical, thermal, appearance, and response to that material, which does not constitute inherently. The development of such multifunctional material enables us to prepare utterly new polymer binary materials that have better properties than that of the conventional composite materials.

Classification of the Multifunctional Composite on the Basis of their Application and Properties

The functionality in the polymeric composites was broadly categorized based on their response to stimuli and applications. Fig. 2 represents the class of the functionality associated with the multifunctional polymer composite.

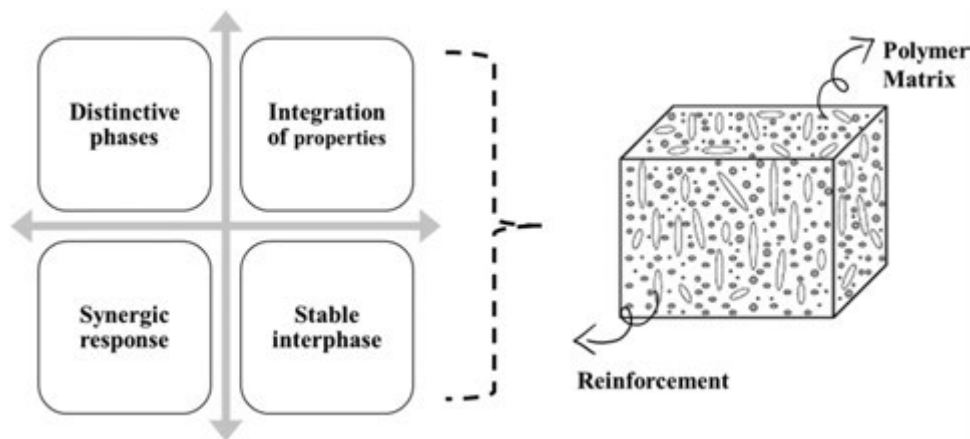


Fig. 1 Fundamental criteria for the multifunctional polymer matrix composite.

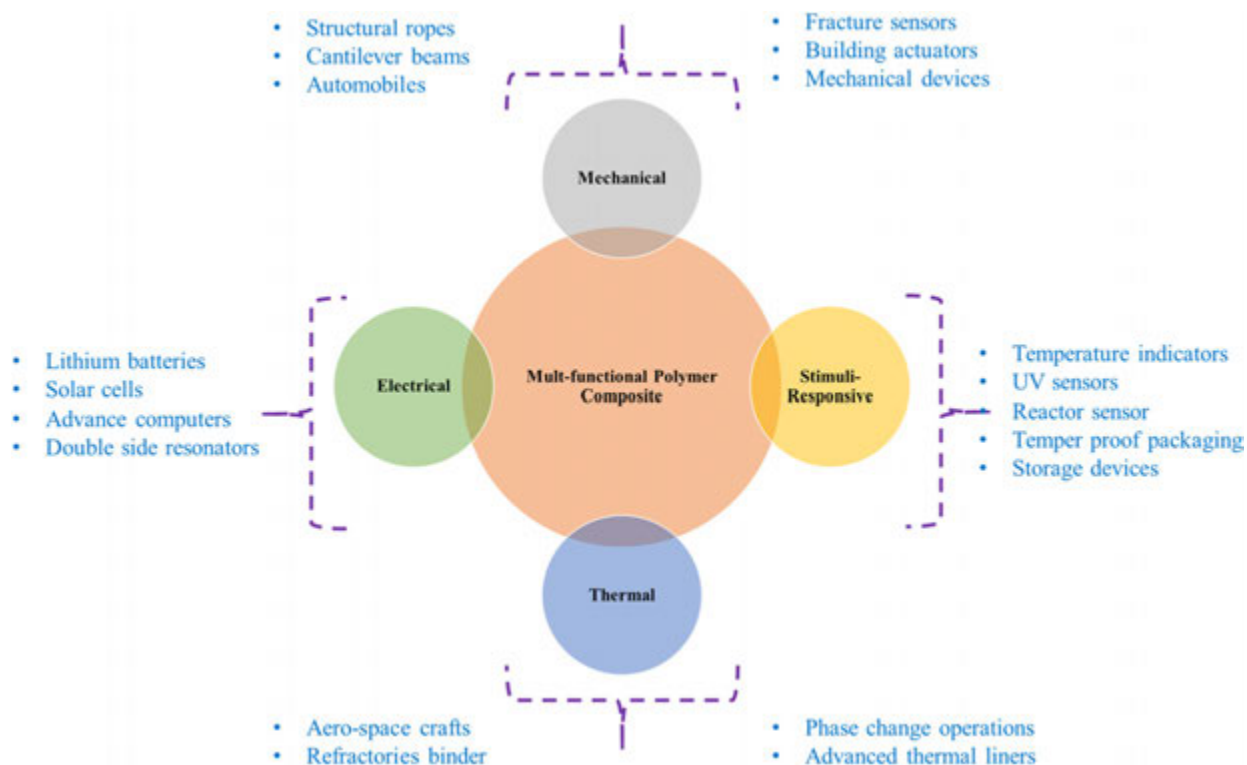


Fig. 2 Nature of functionality associated with the multifunctional polymer composite with their applications.

The multifunctional polymer composites exhibit the combination of the explained properties with high structural stiffness and strength with small values of density. The mechanical based properties combination included the observance of the high strength base material at the adverse condition of temperature and environment. The second class of the which exhibit multiple properties in composites was governed with stimuli-responsive polymer composites. Stimuli-responsive polymer composite rapidly changes their configuration, dimension, or physical properties with small changes in the appropriate stimuli such as heat, pH value, electricity, light, pressure, biochemical, magnetic field, solvent, moisture/water. The third category defines those multifunctional composite which exhibits the inherent strength properties of the material with its excellent thermal stability. This class comprises of those materials which have excellent thermal stability, thermal conductivity, heat absorption tendency, and ability to define the thermal fracture within the structure. The fourth class of multifunctional composites has exhibits the enhanced electrical properties in a combination of chemical stability and strength of the material.

Multifunctional Polymeric Matrix Composite for Mechanical Applications

Multi-functionality polymer composites possess many superior properties such as high-specific strength/stiffness, excellent corrosion resistance, good durability, etc. and thus, they have a considerable potential to be an alternative for the conventional mechanical and constructional base material like steel and concrete. Multi-functionality is the composite reduction in weight, volume, and cost of the mechanical/construction base devices such as girders, beam, king posts, columns and mechanical devices such as like bearing, flywheel, chucks-pin, gear key. All of these forms are used in mechanical and structural applications, but significantly the fibrous and laminates forms are more preferred because of their low density and high design stability.

Structural Component

The structural component requires excellent load-bearing, vibration absorption, and stable dimension properties with low density. The practice of achieving all of these properties in one composite is challenging. Generally, the fiber base composite system implies such properties and thus widely used in the bridge, chains, and road post design. Polyolefin based multifunctional composite exhibits all of these properties, the carbon-based reinforcement like graphene, carbon fiber, and carbon black increases the modulus of the polyolefin systems at minimal doses. This reinforcing structure occupies the interstitial sites in the polyolefin chains. It allows the force to distribute them uniformly in the structure because of which they impart excellent strength without sacrificing the flexibility in the composite. The ultimate tensile strength increased by 56% with the addition of 4% of graphene in HDPE and > 100% in tensile modulus (from 200 to 450 MPa) at 1 wt% graphene loading. HDPE has a linear structure, and the

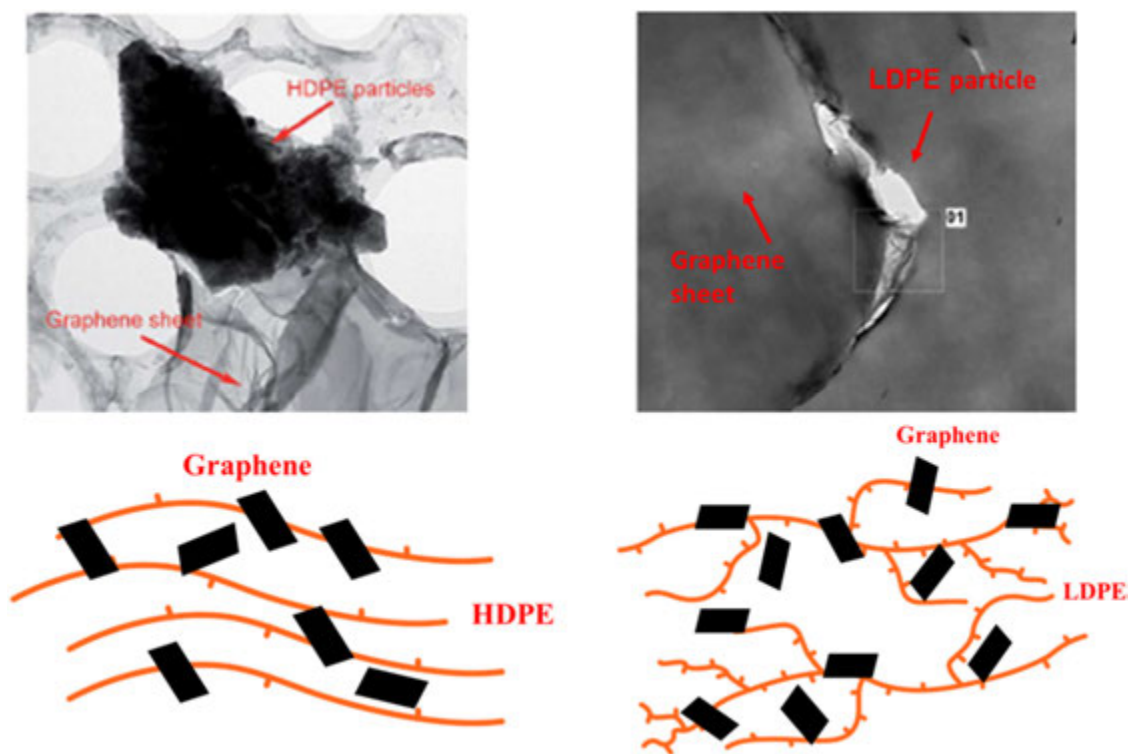


Fig. 3 TEM images and mechanism of the graphene dispersion in the polyethylene – HDPE and LDPE. Reproduced from Wei, P., Bai, S., 2015. Graphene composite with high exfoliation and high mechanical performance via solid-state shear. *RSC Advances* 5, 93697–93705. doi:10.1039/C5RA21271E, with permission Copyright 2017, Royal Society of Chemistry.

graphene moiety acquired a patterned layer like structure, as shown in Fig. 3. The same effect was observed when the LDPE matrix is dispersed with graphene reinforcement. Filling low-density polyethylene by graphite nanoplatelets results in an increase of Young's modulus of the neat LDPE with a slight reduction of the polymer plasticity. The presence of graphene increases the thermal stability, and the dispersion mechanism imparts the incremental strength in the composite, which makes this kind of composite suitable for beam and cantilever applications.

The bridge deck and towers are made from glass fiber reinforced polyester made through the extrusion method, and the stay cables comprise of aramid parallel-lay fiber wound in the polyester matrix for excellent load-bearing capacity as shown in Fig. 4. The polymer matrix allows the stability of the bridge. It prevents crack propagation in winters, whereas the glass fiber reinforcement reduces the weight of the structure and enhance the load-bearing capacity. Similarly, the stable interphase of the composites prevents the vibration transfer within the structure (Stratford, 2012). Because of the facility of attaining the tailor-made properties in such composite, they can be used for the manufacturing of the girders with an intricate design. The combined use of carbon fiber-epoxy (C.F.) and glass fiber-epoxy layer (G.F.) was done in the design of I-shaped girders (Nguyen *et al.*, 2014). The hybridization of the glass and carbon fiber exploits the lightweight and excellent mechanical properties with high vibration absorbing properties. Whereas, the matrix increase in the chemical and corrosive resistance of the composite, which encourages their use in marine construction and temporary cross-bridges exposed to corrosive environmental conditions.

Glass fiber-epoxy with fumed silica composite extremely versatile option for strengthening reinforced concrete structures. Unidirectionally aligned glass fiber has high tensile strength and excellent durability and, therefore, it is logical to consider whether advanced polymer composite materials could be used as part of a structural column to confine the concrete. Fig. 5 shows the application of the wraps over the concrete pillar. The presence of the silica reinforcement prevents the moisture cracking in the pillar and make it suitable for the primer coating.

Sandwiched type composite has its importance in structural applications, having pre-requisite of lightweight and superior mechanical properties. The foam base laminate-composite or layer by layer structures are widely used in iso-thermal panels, support beams, temporary house walls, and pipe support systems. These systems have a core and the layer, layer transmit the applied force in all directions, and core foam reduces the density of the composites. Many of the resin such as phenolic, PVC, PET, PE, PU, and others are widely used for making the core foam base structure. In contrast, polymer-like polycarbonates, epoxy, acrylates, and others were used for the upper layer structure. Fig. 6 expresses the nature of the sandwich multi-functional polymeric composites and their types.

Fig. 7 expresses the multi-functionality associated with the application of sandwich composite in modern structures. A function-integrated GFRP sandwich roof structure for the main gate building shown in Fig. 7(a). The face sheets of this sandwich

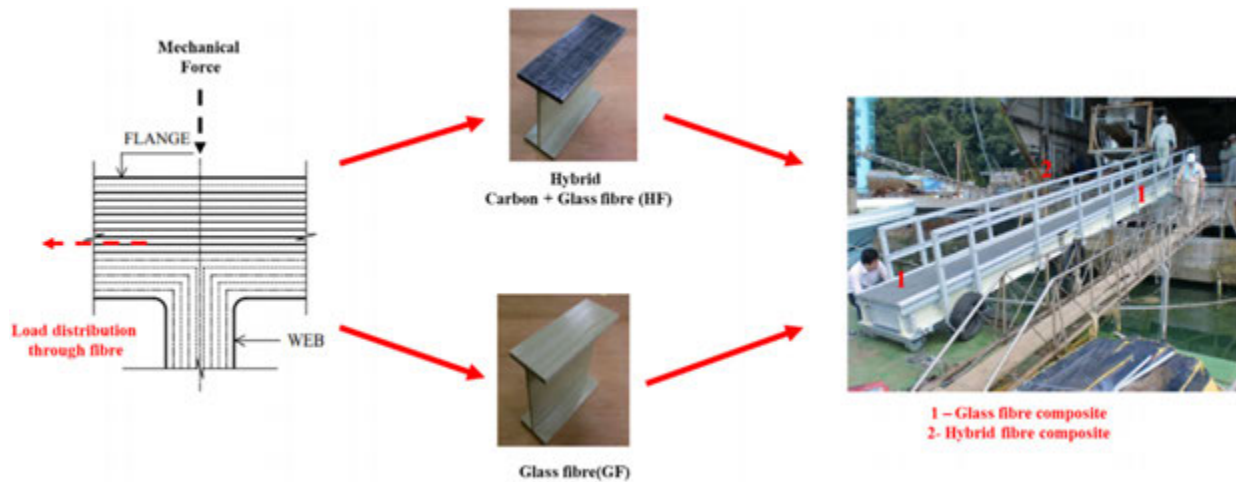


Fig. 4 Details of I-shaped CFRP/GFRP girders and pedestrian bridge using CFRP/GFRP I-girders in fishery harbor in Kure, Hiroshima, Japan, 2011. Reproduced from Nguyen, H., Mutsuyoshi, H., Zatar, W., 2014. Push-out tests for shear connections between UHPFRC slabs and FRP girder. *Composite Structure* 118, 528–547. doi:10.1016/j.compstruct.2014.08.003, with permission Copyright 2017, Elsevier.

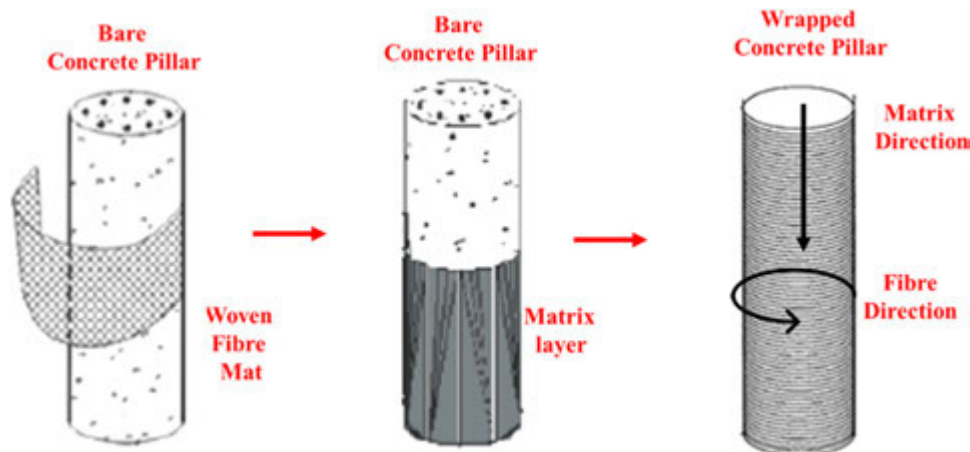


Fig. 5 Application of the silica-infused glass fiber epoxy composite sheets over the concrete pillar.

structure have thicknesses of 6–10.5 mm GFRP, and the core is constructed using up to 600-mm-thick PU foam of three different densities in which a system of crossing GFRP webs is inserted (Keller *et al.*, 2010). The GFRP sandwich systems with ribs represented in Fig. 7(b). These composites were applicable not only for thermal insulation but also as a structural cladding for buildings (Fam and Sharaf, 2010).

Structural Ropes

Ropes and cables are defined as the mechanical component, which transmits the load in the axial direction and supports the moving or dynamic parts of the devices. Ropes comprise multiple components like yarns, fibers, filament, and strands twisted and blocked in each other in linear form. Whereas, in the case of cable, it may have sheath, wire core, cladding, and other multiple reinforcing units. Ibach Bridge in Lucerne Switzerland is the first known structure with actual utilization of the multi-functional composite in cable and rope form. The ropes and the support system of the bridge are made up of polymer matrix reinforced with carbon fiber. The mechanical properties of the carbon fiber over the axial direction are excellent, and because of which, the unidirectional carbon fiber composites acquire 60% strength of carbon fiber in the composite, which is nearly similar to the ultimate tensile strength and modulus of the steel cables. The presence of the carbon fiber imparts low-density properties in the composite ropes.

In contrast, the selection of the suitable polymeric matrix prevents the supporting structure for corrosion and abrasion without sacrificing the flexibility of the composite. Because of its flexibility, such multi-functional composite can form in various arrangements like- lamella, strip loop, rod, twisted loop, and leadline profile. The Neigles carbon fiber reinforced footbridge is the first suspension bridge with multi-functional composite cables in the world. The initial footbridge was constructed with steel

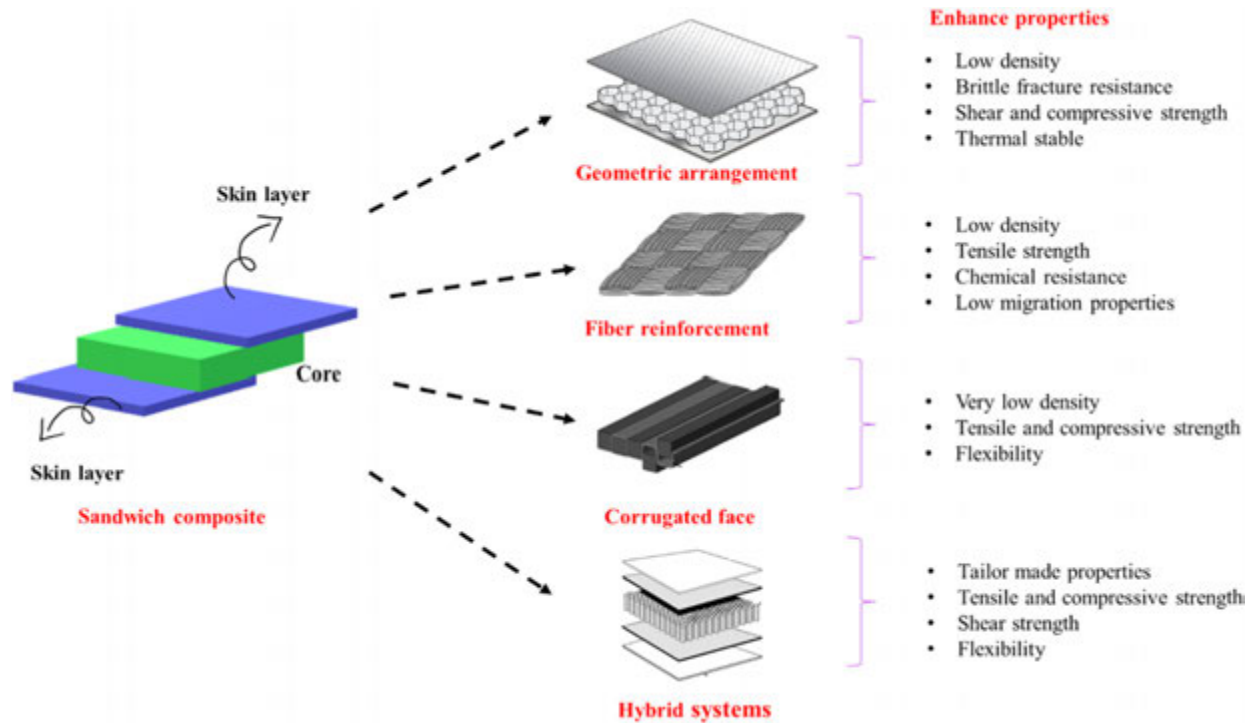


Fig. 6 Nature of the sandwich multi-functional polymeric composites and their types.

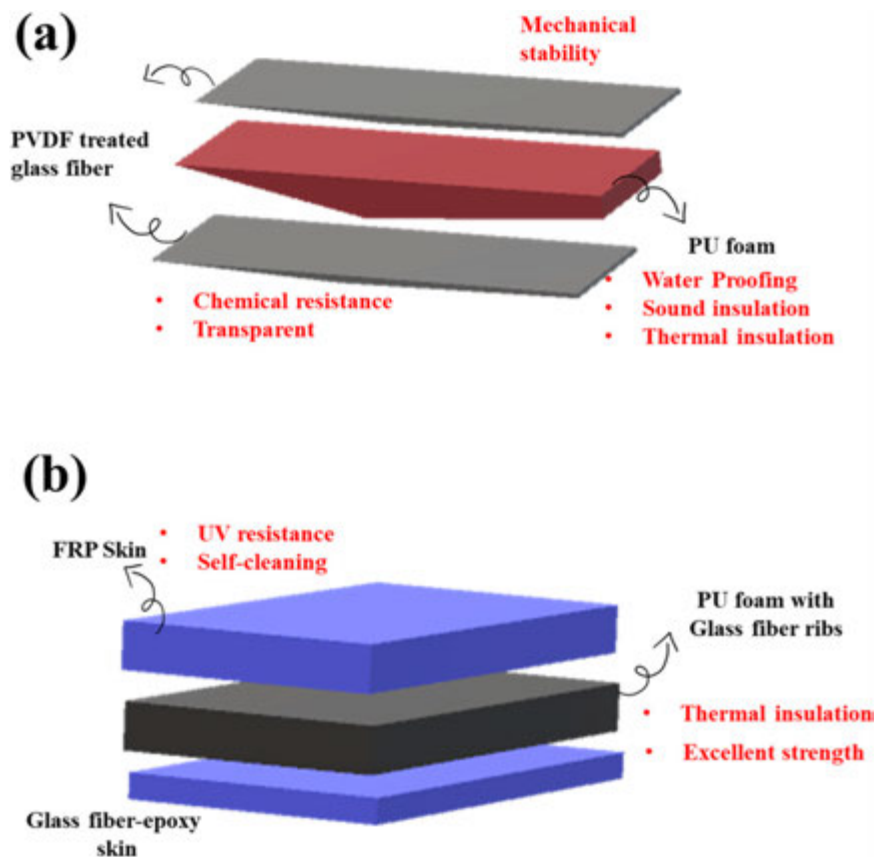


Fig. 7 Multi-functionality associated with the application of sandwich composite (a) Roof laminate and (b) Indoor walls.

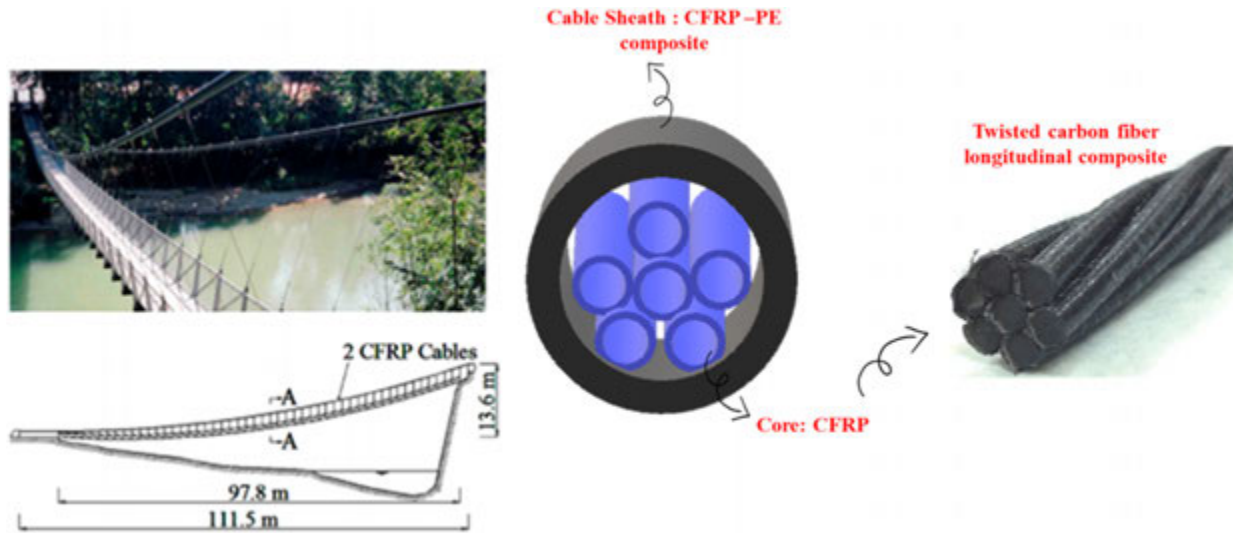


Fig. 8 Structural design of the bridge with the CRPF cable arrangement of Neigles. Reproduced with permission Copyright 2017, Elsevier.

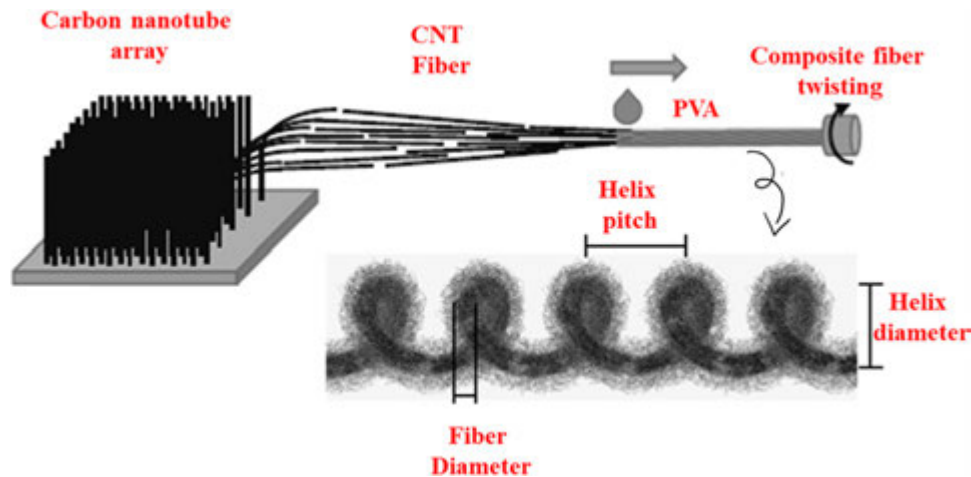


Fig. 9 Illustration of the PVA-carbon nano-tube based super stretchable composite cable. Reproduced with permission Copyright 2017, Elsevier.

cables. However, due to the severe corrosion, the main steel cables were removed and replaced with CFRP cables. **Fig. 8** shows the structural design of the bridge with the CRPF cable arrangement (Liu *et al.*, 2015).

The multi-functional nanocomposite also contributes to the construction cable application. Carbon nanotube-PVA based cables have excellent flexibility with super stretchable nature, and thus these composites are the best candidates for the pillar padding and river defense devices. Stated carbon nano-tube and PVA composite cables have the maximum tensile strength between 350 and 380 MPa similar to spring and tensile strain in the range of 220%–250%. **Fig. 9** indicates the spring-like behavior of the cable formed with carbon nano-tube reinforcement. The free helical structures based on CNT fibers have been shown to possess the desirable stretchability. At the same time, the PVA matrix prevents the wrinkling effect in the composite, and thus, it makes the composite desirable for force damping or absorbing application in construction industries (Liu *et al.*, 2017).

Mechanical Devices

The mechanical devices include industrial dryers, separators, transmission units, spacers, heat exchangers, bushings, fitting units, etc. All of these applications are exposed to a large amount of mechanical force, torque, impulse, and vibrations. Recently, most such devices comprise of the multi-functional polymer composite. Polymeric composite acquires all of the required properties. On top of it, they have low density and excellent tribological properties. This makes the device light and easy to transport, ship, and install in the prescribes space of utility.

The 40% nylon 6 fiber-filled polyoxymethylene composite has excellent dimensional stability with a low thermal expansion coefficient and widely used in the gear application. Still, because of the susceptibility towards wear and abrasion, such gears are

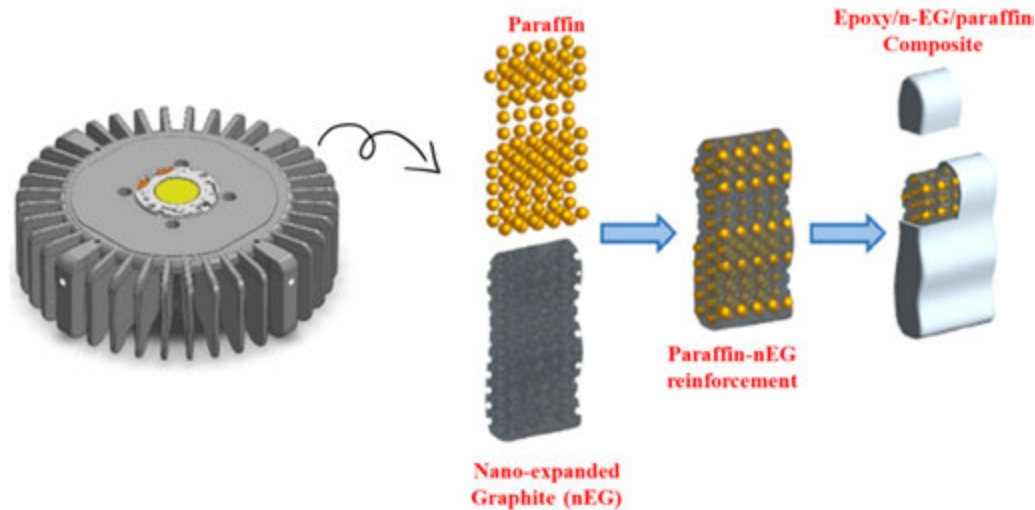


Fig. 10 Illustration of the epoxy reinforced with nano expanded graphite and paraffin composite. Reproduced with permission Copyright 2017, Elsevier.

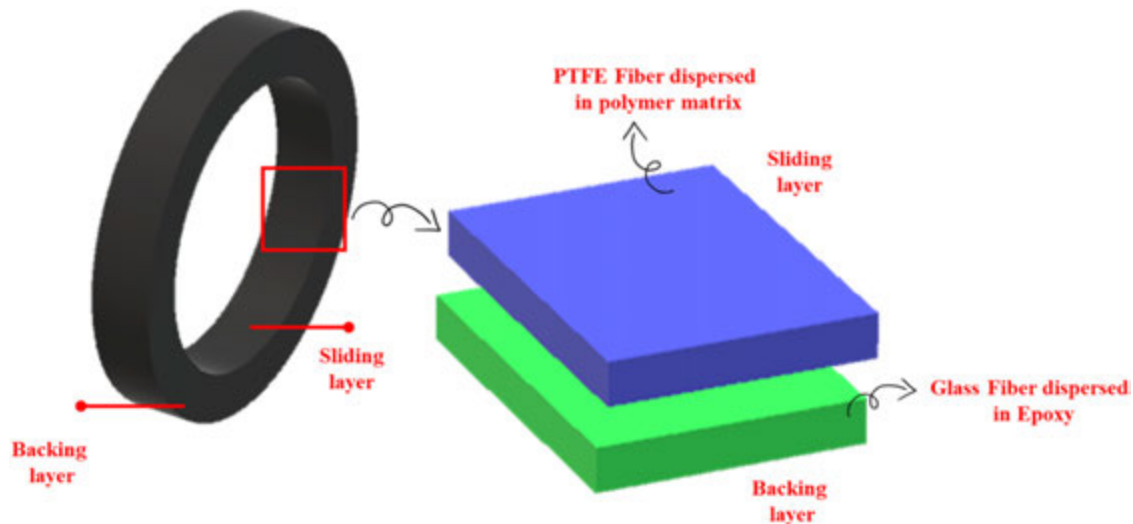


Fig. 11 Design of Epoxy bushing reinforced with PTFE fiber layer and glass fiber layer.

only limited to the small size and power transmission within a small range. Reinforced nylon 6/6 with 20% short glass fiber imparts excellent wear and tear resistance in the injection-molded gear. Still, because of the suitability toward the moisture absorption, such gear applications are limited to controlled atmospheric conditions. Polyoxymethylene matrix reinforced with PEEK and glass fiber resolve the problem and provide excellent tribological, mechanical, and structural properties to the gear with dimensional stability under normal conditions. Fig. 10 shows the composition of the gear and the structure of the PCM in the epoxy expanded graphite matrix (Wang *et al.*, 2017).

In the composites, the paraffin and expanded graphite are uniformly dispersed into the network of epoxy resin, which acts as a latent heat storage material while the epoxy resin as a supporting material which provides stability to the transmission system. Multi-wall materials like nanorods, nano-tubes, and layer structural also help to enhance the properties of the composite. One of its examples is multi-wall carbon nano-tubes (MWCNTs) reinforced polyphenylene sulfide. Polyphenylene sulfide (PPS) with acid modification is reinforced with multi-wall carbon nano-tubes, short carbon fiber, and graphite. The composite was manufactured through the extrusion process and formed into the shape of bearing through injection molding operation. The MWCNT increases the thermal suitability of the composite and restricts the radial thermal expansion in the bearing. The graphene allows the self-lubrication in the bearing with the imposition of the mechanical strength.

As of the short fiber reinforcement, the continuous fiber reinforcement allows a higher fiber volume fraction and results in a much higher load-bearing capacity than the short fiber reinforced alternatives. Because of which the composite for device bushes requires the design of such a multi-functional system that qualifies the fundamental need of the mechanical bushings. Bushings majorly comprise two distinct layers, as shown in Fig. 11. The primary layer consists of a high-volume fraction of glass fibers, and

the second layer is made of PTFE- and other polymer fibers. The first layer has a function of embedding the excellent mechanical properties in the composite and prevent the bushing from the radial deformation. Whereas, the secondary of the PTFE imparts low coefficient of friction. Both of these layers are encapsulated within the epoxy matrix. The interaction between the two layers allows the absorption of the suddenly applied force and increases the impact resistance of the composite with prevention to edge loading and misalignment. The PTFE fiber layer increases the inertness of the structure and provides excellent resistance to bushing form corrosive media. The epoxy matrix and the first layer of the structure absorb the noise and vibrations. Because of this, the bushing can sustain with bearing capacity under low sliding speeds (less than 0.01 m/s) can be up to 150 MPa.

Self-lubricating polymer composite with excellent mechanical properties components is often needed in machine systems in which no external oil or grease lubrication is acceptable. One example is the use of sliding shoes in textile dryers. To such an application, the polycarbonate filled with PEEK and graphite flakes with PTFE additive system shows excellent toughness and with continuous loop sliding strength without any deformation in the composite.

Other

- (1) *Smart roofs*: The multi-functional composite of an epoxy matrix reinforced with jute and glass fiber is widely used in the design of the smart roofs. The long jute fibers were impregnated with the woven sheets of glass fiber cured with silane-modified unsaturated polyester resin. The 15% randomly dispersed jute fiber enhances the noise-damping properties of the roof, whereas 15% of the woven mat of glass fiber incorporates the thermal insulation in the roof (Aly-Hassan, 2015). In contrast, the hydrophobic or snow repellent functionality is induced by the modified unsaturated polyester matrix. In addition to it, the hybrid of the random and woven arrangement of the fiber encourages the uniform distribution of load within the structure.
- (2) *Pipe Coatings*: Polypropylene matrix reinforced with expanded graphite composite have excellent mechanical properties with high abrasion resistance towards soil particles and have the capability if machining such composites are widely used in onshore pipe coatings.
- (3) *Desalination membranes*: Polyaniline and carbon nano tubes-based composite was deposited over the fabric, which provides the membrane for desalination. The electroactive property of the matrix and the mechanical stability of the carbon nano-tubes enables the composite for ion electro-sorption and storage.
- (4) *Electrostatic discharge proof mechanical devices*: CNT-filled conductive ABS nanocomposites, finding a low CNT concentration for electrical conduction (0.75 wt%), though limited to a much lower final nanocomposite conductivity of 10 – 5S/m, suitable for ESD protection applications.

Multifunctional Polymeric Matrix Composite With Stimuli-Responsive Application

Stimuli-responsive polymeric composite reveals multiple properties that are governed with switch effect. The switch for expressing the property is called stimuli, and the change in properties of the polymeric composite is termed as the response.

So, the polymeric material which reciprocates the stimuli with a change in their physical or chemical properties falls under this class of material. Broadly the response is classified in physical and chemical classes. Fig. 12 depicts the relation of stimuli and response with the state of composite (gel, solid, surface, and liquid). In such polymeric composites, one can achieve one or more synergic response by multiple stimuli, or multiple stimuli through single stimuli.

Sensors

Modern industries comprise the challenging process where efficiency, nature, and safety are the key aspects. In such a challenging process, the evaluation of its sustainability will not be possible in the absence of smart composites. Such smart composites are widely used in sensors application because of their three fundamental properties (1) Ability to sense the stimuli in adverse environmental conditions, (2) converting stimuli in response in the real-time interval, and (3) making actuation by moving away from or to the stimuli. Because of these three attributes, such smart composites are widely used in sensing and monitoring of structure health, drug delivery in humans, gas sensors, fire safety alarms, chemical processing flow meters, humidity sensors, etc. The first thermal sensor-based composite was introduced commercially in the form of fluorescent thermometers. Fluorescent thermometers contain polyacrylamide matrix incorporated with metallic nano-particles and 4-N-(2-acryloyloxyethyl)-N-methylamino-7-(N, N-dimethylamino)sulfonyl-2,1,3 benzoxadiazole pigments. The metallic nano-particle allows for enhancing the thermal conductivity of the system. By sensing the temperature, the polyacrylamide chains undergo the LCST transition and allow the pigment to participate in the molecule conjugation. As a result, the pigment shows the change in their color, and by sensing that change, the temperature was recorded.

The layer by layer multi-functional composite of polyurethane (PU)- single-wall carbon nano-tube and poly(3,4-ethylene-dioxythiophene) (PEDOT) polystyrene sulfonate(PSS)-single-wall carbon nano-tube exhibits excellent transparency, stretchability, and response to strain. The sensor acquires 112% elongation, 62% optical clarity, and GF ¼ 62 high sensitivity. This strain sensor can be used to detect the emotional expressions, such as laughing and crying, by attaching it to the face of the human.

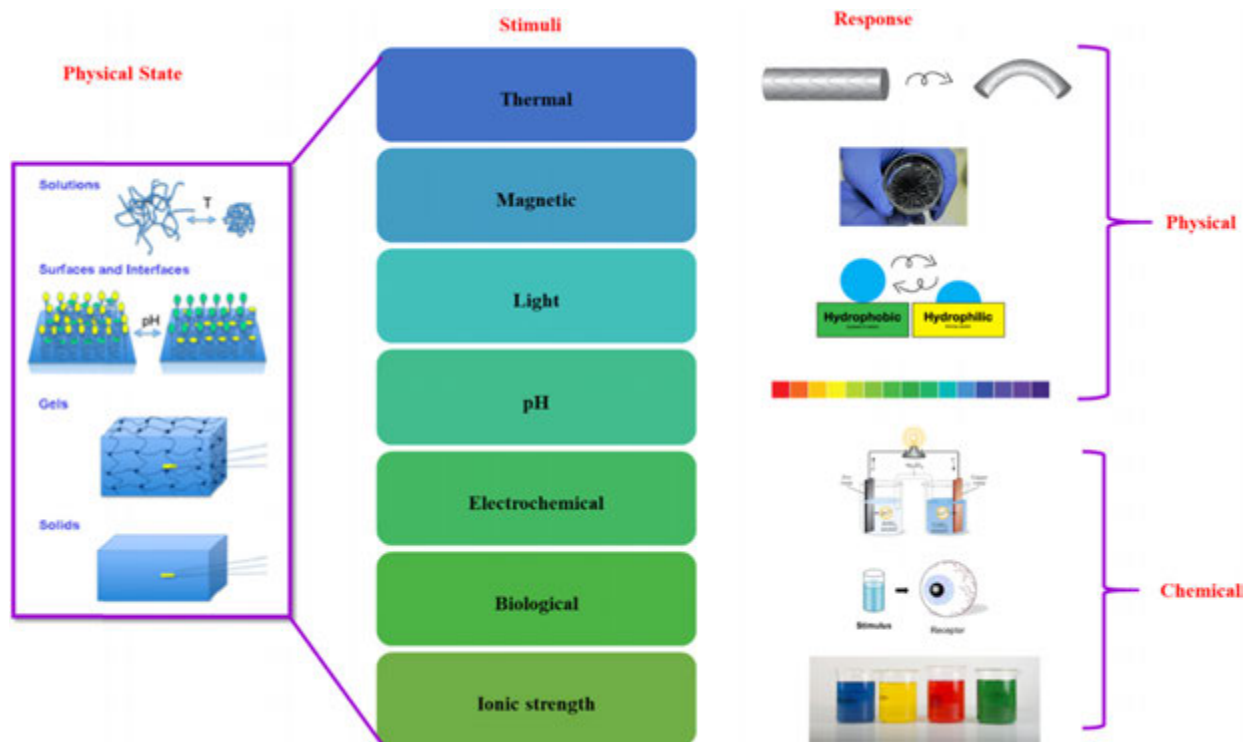


Fig. 12 Relation of stimuli and response with the state of composite.

An interesting example is a sensor in which poly(*p*-phenylene vinylene) was used as a dye. The dye was incorporated in LDPE through the melt-encapsulation method. The LDPE was filled with talc nano-particle as the particulate reinforcement. The added dye showed the stress damage area when the sample was characterized by luminescence during stretching in the universal testing machine. The talc particle creates the epicenter for the force transmission in the LDPE matrix, and this force transmission allows the breakage of the dye encapsulation. Because of which the composite indicates the stress damage in the structure.

Smart composites or multi-functional responsive polymeric composite also considered as an excellent choice for biosensors. Biosensors are the monitoring devices that detect the chemical substance or biological with the human, animal, and plant body and record the change with the help of physicochemical detectors. In modern health technologies, such sensors are the game changers in many applications. For example, composite of Fe_3O_4 – poly(Indole-*co*-thiophene), where magnetic Fe_3O_4 is in a particulate nano form, provides the center for electromagnetic sensing and matrix poly(indole-*co*-thiophene) allows the conductivity of the signal through it. Such a stimuli-response base composite is widely used in the hemoglobin diagnostic biosensor (Rouhi *et al.*, 2016). In the sensor comprises of the carbon paste electrode modified poly(Indole-*co*-thiophene)- Fe_3O_4 nano-composite, the composite immobilizes the hemoglobin in the blood by responding through the change in electrical signals. **Table 1** represents examples of polymeric and reinforcing systems used in the biosensor applications.

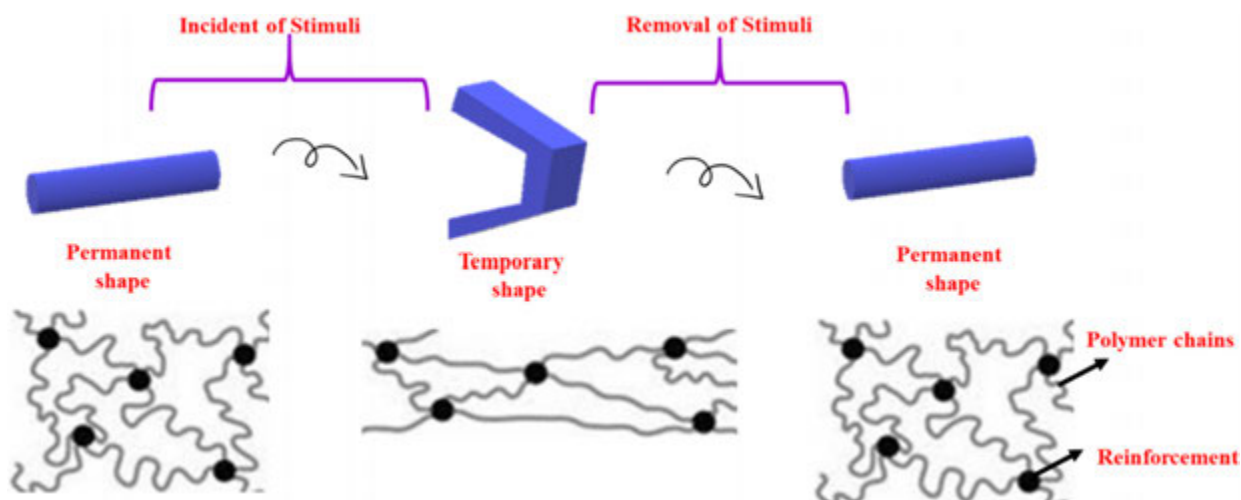
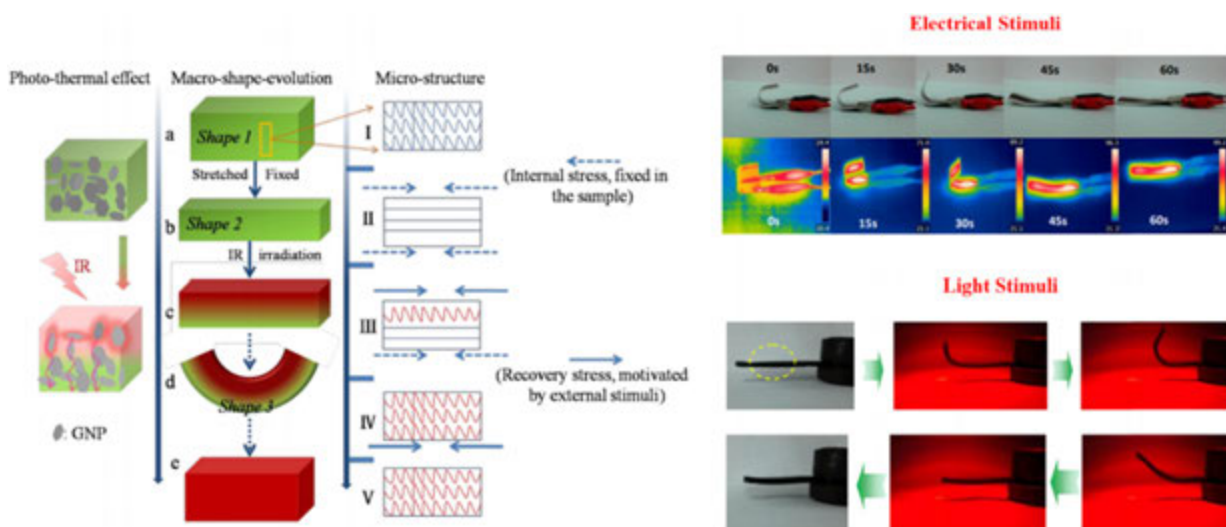
Shape Memory Application

The original phenomenon of shape memory was established with the martensite, and that is the reason it is also termed as martensitic transformations. In a polymer, these effects can be seen because of the interaction of the crystalline and amorphous phase. Such polymer matrix composites exhibit a unique property of showing transformational responses, when subjected to heating, exposed to light, on the application of pressure, placed under an electric and magnetic field, as shown in **Fig. 13**.

The shape memory polymer composite act as smart materials possessing a tendency to regain their original permanent or partially deformed shape on the application of external stimuli in the form of heating, electric or magnetic field, or by light stimulation. The effect of the shape memory can be seen by determining the bending, shrinkage, and deformation in the composite when exposed to stimuli. For example, the composite of cross-linked polyethylene and silica particle shows large deformation when subjected to heat stimuli. Similarly, after removing the stimuli, the composite shows equivalent recovery in the structure. Because of such multi-functional of the composite, they are readily used in the electric wiring, shrink film, and conduct application. The multi-functional composite of poly(caprolactone) (PCL)/polyurethane (PU) blend with graphene nanoplatelets reinforcement shows the shape memory effect for light and electrical stimuli. **Fig. 14** shows the graphical abstract of the shape memory effect in PCL-PU/graphene composite. The graphene molecules allow the light and electrical actuation in the composite. In contrast, the presence of PCL interferes with the crystallinity of the matrix in combination with the soft and hard segment of the

Table 1 Various examples of polymeric composites used in biosensors

Sr. No	Matrix	Reinforcement	Application	Detection	Reference
1	Poly(o-phenylenediamine)	Graphene and gold nano-sheets	Detection of carcinoembryonic antigen	Electro-chemical change	(Chen <i>et al.</i> , 2013)
2	Teflon	Multi-wall carbon nano-tube	Detection of glucose and ethanol	Electro-chemical change	(Wang and Musameh, 2003)
3	Polypyrrole-polyaniline	Gold nano-particle	DNA sensing	immobilization of acid	(Wilson <i>et al.</i> , 2012)
4	Chitosan	layered double hydroxides	Phenol Sensor	Enzyme electrode base immobilization	(Han <i>et al.</i> , 2007)

**Fig. 13** Schematic diagram of shape memory polymer composites.**Fig. 14** Graphical abstract of the deformation mechanism of the electrical and light-activated shape memory PU/PCL-graphene multi-functional composite. Reproduced with permission Copyright 2017, American Society of Civil Engineers.

PU phase. Because of which when these composites are exposed to the stimuli, the structural arrangement of the phase changes and causes the transformation in shape.

Unidirectional carbon fiber reinforced epoxy shape memory composite express excellent shape memory effect induced by thermal energy. The composite was transformed into temporary shape at 120°C, and shape fixation was done at 20°C. Because of

Table 2 Application of multi-functional stimuli-responsive polymeric composites

Sr. No	Matrix phase	Reinforcing phase	Application	Reference
1	Chitosan	Bio-active glass nano-particle	Bone defect fillers	(Correia <i>et al.</i> , 2015)
2	Polyacrylates	Acrylic fiber with cellulose	Thrombectomy devices	(Muschenborn <i>et al.</i> , 2014)
3	PTFE	Nylon fibers	Kidney dialysis needles	(Ortega <i>et al.</i> , 2007)
4	Polyurethane	Graphene oxide	Erasable Braille	(Agronin, 2000)
5	Polyester(PET-Cellulose)	Multi-wall carbon nano-tube	Pressure garments	(Gök <i>et al.</i> , 2015; Holschuh <i>et al.</i> , 2015)
6	Epoxy, PU, PE, and Polyesters	Carbon black, graphene, carbon fiber	Deployable structures	(Santo <i>et al.</i> , 2014)
7	Epoxy	Carbon black	Self-peeling dry adhesive	(Eisenhaure and Kim, 2014)

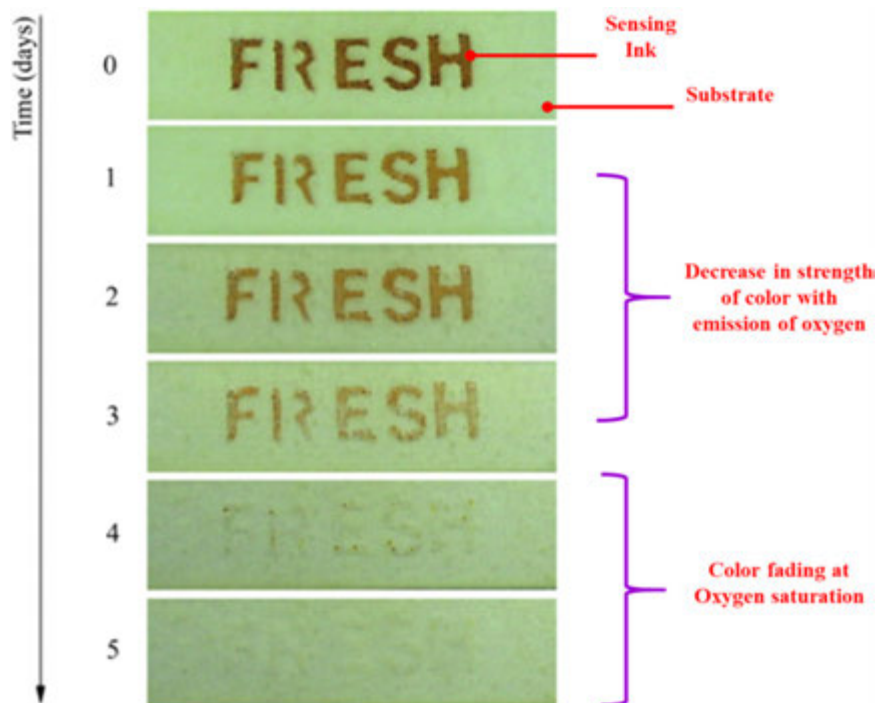


Fig. 15 Polyacrylate - anthraquinone-2-sulfonic acid-modified hydroxypropyl cellulose composite ink coating for freshness sensing applications. Reproduced from Boscher, N.D., Bohn, T., Heier, P., Moisy, F., Choquet, P., 2013. Optical sensing responses of Cr(III)Cl₃(TPP)(H₂O)-based coatings obtained by an atmospheric pressure plasma method – Application to the detection of volatile. *Sensors & Actuators: B. Chemical* 191, 553–560. doi:10.1016/j.snb.2013.10.044, with permission Copyright 2017, Elsevier.

the balanced cross-linked and linear phase, the composite offered 96% recovery to its permanent shape. **Table 2** express the nature of matrix and reinforcement used in the shape memory composite for a specific application.

Smart Packaging

Packaging enhances the shelf life of any product by protecting the product against deteriorative effects caused by exposure to and interaction with the external environment. To satisfy the need of the consumer in the present world, packaging industries have to rely on active, stable, and intelligent packaging structures and materials. Those a packaging system that is capable of carrying out intelligent functions (such as sensing, detecting, tracking, recording, and communicating) to facilitate decision-making to extend shelf life, improve quality, enhance safety, provide information, and warn about potential problems are classified as “Smart packaging”.

Polyacrylate based composite reinforced with anthraquinone-2-sulfonic acid-modified hydroxypropyl cellulose will act as sensing ink for oxygen emission. **Fig. 15** shows the prototype of such a device, where the ink over the label having polyacrylate/cellulose composite fades out with a decrease in the freshness of the product. Temperature responsive polymeric composite like thermoplastic polyurethane-modified talc are materials with great importance in cases of meat, dairy products, and frozen food storage.

Additionally, the rate of Physico-chemical and microbiological changes is highly dependent on temperature values. During storage, the changes in metabolite concentrations such as glucose, amine, ethanol, organic acid, CO₂, TVB-N, adenosine triphosphate degradation products, and biogenic amines indicate spoilage of meat products. Likewise, in the meat storage packaging, the detection of volatile amine can sense the spoilage of the meat. Polyethylene terephthalate- PET fiber base composite added with metalloporphyrin has a wider range of applications in the meat packaging sector. Such indicators observed the volatile component and then convert the gas stimuli into color response (Biji *et al.*, 2015).

Moisture is the other important factor responsible for food spoilage; it provides a bacterial friendly atmosphere, and thus bacteria reproduce in such atmospheres, so to increase the life of the food, it is very important to suppress the water activity in the product. For example, the cheese and candies packaging uses the PP/Talc/molecular sieve base composite structure, which increases the life of the product by 30%. In many of the cases, sandwich laminates of polymer and metallic layers are also used. Still, because of limitations in their recycling, such laminates are not part of the sustainable technologies.

Milk packaging has been newly developed to evaluate the degree of milk spoilage during storage, mainly due to increased demands on product safety, shelf-life extension, and customer convenience. Nowadays, multi-functional polymeric composite layers or laminates are widely used in this are the composite of PP and ion-exchange resin-modified clay exhibit the spoilage sensing capabilities in milk packaging. Quaternary alkylammonium cations treated clay sense the pH change in the milk and thus respond to this change by converting its color from green to yellow (Tassanawat *et al.*, 2007).

Others

Self-healing

Polymer composite with multi-functional properties exhibits tremendous application in the engineering field under adverse environmental conditions. Because of the continuous exposure to such harsh conditions, many of the polymeric composites are susceptible to micro-cracking and brittle failure. To avoid this failure, such composites are required, which can repair the formed crack inherently, and such composites are called as self-healing composites. The stimuli can be of redox, thermal, light, magnetic, etc. but the response mechanism complies with the filling of the micro-cracks and cause healing of the composite. For example, polyvinyl butyral (PVB) composite having a 3-Nitrosalicylic acid monomer having redox-sensitive polyaniline (PANI) shell. This composite system was coated over zinc panel, when shell senses corrosion, the PANI shell switch from impermeable to permeable when there is a change in potential concurrent, to release the active agents in the crack, because of which the monomer start polymerizing within the crack (Vimalanandan *et al.*, 2013). Similarly, epoxy composite with hexamethylene diisocyanate filled polyurethane capsules senses the tribological stimuli or wear and tear failure. The wear and tear in the capsule allow the release of the monomer to cause repair of the crack (Khun *et al.*, 2014). A hybrid carbon-fiber/epoxy composite reinforced with self-healing core-shell nanofibers at interfaces was fabricated by co-electrospinning, where the healing agent DCPD was encapsulated into polyacrylonitrile (PAN) to form core-shell DCPD/PAN nanofibers activated by heat.

Drug delivery

In recent years, pharmaceutical research has focused in field of drug delivery. Currently, the use of multi-functional polymer composite represents an alternative system with a huge potential for the targeted distribution of drugs or biological macromolecules in the body. Magnetic nanoparticles based polymer composites are sensitive to the external alternating magnetic field. It is used frequently in nanocomposite to control drug release. Poly(lactide-co-glycolide acid) microparticles loaded with both insulin and magnetite nanocrystals. The magnetic particle guides the drug under the influence of the magnetic field in the area of the small intestine and helps to control the blood sugar in the body.

Chitosan reduced graphene oxide nanocomposite was prepared through a reduction process and was used in the transdermal drug carrier system. The reduced graphene enhances the electrical conductivity of chitosan and makes the nanocomposites useful for electroporation or iontophoresis drug delivery applications.

Similarly, the UHMWPE-CNT composite has the capability of loading and release the drug to the targeted area. CNTs reinforced PE composite surface is modified through chemical etching technique. Etching causes the creation of porous structure in the polymeric matrix; these interconnected micropores provide the space for the drug accumulation and allows the acetabular cup to release the drug on the targeted area.

Ag/carboxymethyl cellulose-poly acrylamide hydrogel nanocomposite has biodegradable behavior. They have studied the nanocomposites with diclofenac sodium (DS) as a model drug to assess the release characteristics. According to the research outcome, the synthesized matrix has shown safe transmission of drugs through the stomach (high acidic environment) without any alterations and efficient release of drug components under the basic environment of colon.

Composite of polylactic acid- poly(ethylene oxide) imbedded with polysaccharide base microcapsule carrying bromelain drug detects the change in enzymatic atmosphere and delivers the drug to the targeted area. Clay-based reinforcement also expresses application in the drug delivery segment. Aluminosilicate in the form of halloysite nanostructure dispersed in the hydrogel of sodium hyaluronate (SA)/poly (hydroxyethyl methacrylate) and embedded with the anticancer drug is widely used for treating spot cancer.

Multifunctional Polymeric Matrix Composite With Thermal Application

Fire-Safety Devices

Multi-functionality in polymeric matrix composite enables their use in critical applications where the material has to sustain the strength in the adverse condition of temperature and environment. Although, the fire resistance of such composite alarms the severe safety issues. All of such composites have polymeric matrix, vulnerable to combustion when exposed to direct contact of fire. To incorporate the flame retardancy in the composite mainly, two approaches are implied – (1) modification of polymer matrix/fiber with flame retardant functionality and (2) Addition of the flame-retardant additive in the composite systems. Both approaches are based on the elimination principle. The main aim of this principle is to eliminate any of one entity required for the combustion.

For example, Metal oxides and hydroxide modification in composite follows the heat sink mechanism and suppress the heat gradient because of which arrest the combustion in the composite. Boron based modification forms the char around the composite and eliminates the air supply required for the combustion. The synergistic base modification allows the combination of char formation of gas-phase to eliminate the air and direct contact with the fuel. The grafting of polypropylene with acryl-amide (AAM) enhances the flame retardancy in the composite. The acryl-amide allows the formation of char when it comes in direct contact of fire and prevents the burning of the plastic.

Similarly, grafting of brominated monomer either on the polypropylene matrix or on glass fiber by polymerizing around the Sb_2O_3 particles or onto both. In continuation of the grafting, the metal oxides were also incorporated in the system, which increases the flame retardancy properties of the composite. The phosphorus moieties were incorporated in the main chain of PET, and the composite was reinforced with glass fiber. Glass fiber enhances the thermal management capabilities of the composite. In contrast, the presence of phosphorus in the main chain suppresses the burning tendency of the composite. It was observed that GF-PET composite achieved V-0 rating in the UL94 test when 15% FR-agent was added while the LOI increases linearly with increasing FR-agent add on up to 26% where it achieves an LOI value of 32. In addition to this, the glass fiber also increases the tensile modulus of the composite. It fits the composite for potential applications in devices like electrical laminates, sparks plug casing, and in other electrical applications. Carbon microspheres also impart the flame-retardant nature in the PET matrix.

The flame-retardant nature of the composite is also acquired by grafting inorganic salt on the main chain of thermoplastic polymer and reinforcing the polymer with inorganic filler like glass fiber and carbon fiber. The inorganic salt like include alkaline earth salts and alkali metal salts decompose at elevated temperatures to produce an insulating and adherent char on the polymer surface that provides fire protection. In addition, the decomposition reaction of the salts produces a significant amount of carbon dioxide that serves to quench the flame. The typical example is ABS composite, ABS is added with 21% sodium methacrylate salt through graft copolymerization method. Because of the flame-retardant moiety present in the main chain ABS the time-to-ignition of the composite increases by 161% (Suzuki and Wilkie, 1995).

Thermoplastic like polystyrene, PP, and polyacrylonitrile matrix can be incorporated with Silicon-methoxide-modified clays reinforcement. The linkage between the silicon and clay occurs in the clay. Still, it is not likely to occur in the nanocomposite, perhaps because of the presence of the polystyrene increases the distance between the reactive sites and the cation cannot span this distance, which decreases the heat release rate of the composite and made it more suitable for electrical and automobile applications (Zhu *et al.*, 2002).

A new type of epoxy composite was made by cross-linking diglycidyl ether of braided carbon fibers (CFs) and bisphenol A-epoxy matrix modified by phosphoric acid. The phosphorus acid in the structure of modified epoxy allows the formation of a condensed phase and reduces the total heat release in the combustion. The flame-retardant nature in the epoxy can also be incorporated by reinforcing the matrix with graphene nanosheets (GNs) modified by molybdenum disulfide (MoS_2). Compared with neat epoxy, the thermal stability of $\text{MoS}_2/\text{GNS}/\text{Epoxy}$ composites with 2.0 wt% MoS_2/GNS mass fraction was significantly improved, initial decomposition temperature increased by 53°C . HRR and THR decreased by 45.8% and 25.3%, respectively, and the TSR was reduced by 30.5% (Wang *et al.*, 2013).

The combination of clay and carbon nanotube is also one of the most widely used flame retardant reinforcement for the epoxy matrix. Fluorinated montmorillonite with multi-wall carbon nanotube -epoxy composite exhibit gas phase mechanism of the flame retardancy. The thermal insulation of MMT and the high specific heat of MWCNT hindered the heat transfer of EP. The char yield increased from 9.1% to 15.4%, and LOI grew from 21% to 31% due to the influence of flame retardants.

Aerospace Application

Aerospace industries demand the development of such material that can sustain its property in an adverse environment of space without any deformation. In addition to it, the material should have low density so that it not affects the carriage capacity of the launch vehicle and thus multi-functional polymeric composite are the best suitable option which can sustain its properties when exposed to high vacuum, ultra-high or low-temperature cycle effect, ultraviolet (UV) radiation and ozone saturation conditions. Carbon fiber and polyether amide matrix-based composites added with graphene nanoparticles are progressively being employed in spacecraft and aircraft industry because of remarkably high strength, modulus, lightweight, good fatigue life, high stiffness, and excellent corrosion resistance. Similarly, thermoplastic polymer matrix like aromatic polyimides is known to have excellent properties such as high dimensional stability, low thermal expansion, and outstanding thermal and environmental stability due to

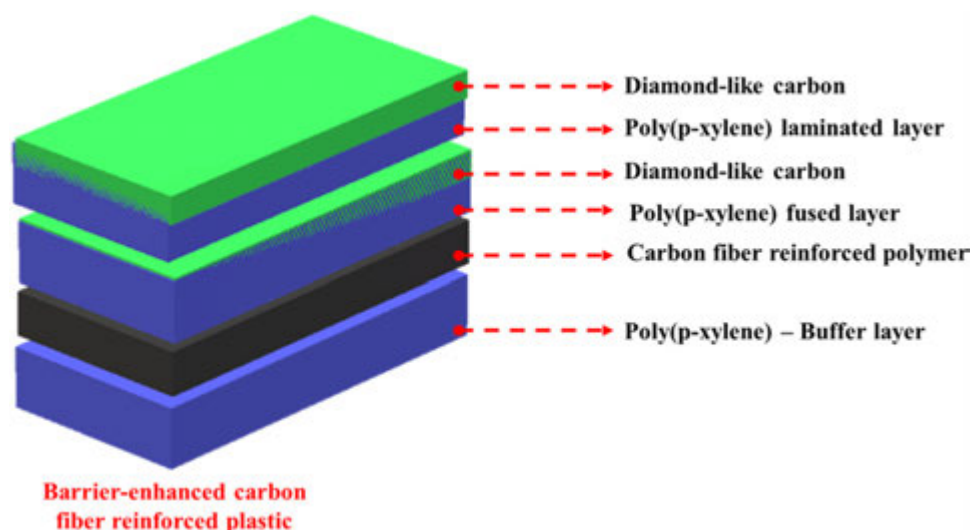


Fig. 16 Structure of BECFRP composite used in satellite camera mounting.

which such matrix base composite are widely used in the rocket grid, fuel tank casing, jointing of the aircraft laminates and in the fuel cell or batteries.

Polyetheretherketone (PEEK)-carbon fiber-based laminates show excellent mechanical properties with extensive heat resistance capabilities. The advantages of PEEK material over traditionally used CFRP material are in terms of lightweight, low surface root means square (RMS) error and its applications for reconfigurable space antenna (Kalra *et al.*, 2019). PEEK matrix base composite can save between 10%–45% in the overall weight of the structure. In addition to it, PEEK has a low thermal expansion coefficient as compared to aluminum and thus suitable for high-frequency band antennas with high surface accuracy. Ultra High Molecular Weight Polyethylene (UHMWPE) with glass fiber-epoxy. The composite produced gives excellent shielding and protection against chlorine-based radiations along with enhanced mechanical properties of structural blanket applications. Thermal blankets are essential for regulating the temperature of most spacecraft. PVDF filled silica nanoparticle-based composite has excellent chemical inertness. The cross-linked matrix of vinylidene fluoride (PVDF) has been developed for wire and cable insulations for high radiation environments. Applications include RTGs (Radio-isotope Thermal Generators) and high radiation environments such as Jupiter orbiters.

The blankets consist of a polymer film that is either, (1) filled with carbon black pigment to absorb sunlight, or (2) coated with a layer of vapor-deposited aluminum to reflect sunlight. The layers are made up of polyethylene terephthalate and polyimides separated by fine scrim cloths made from polyamide. The thin layer was reinforced with indium tin oxide particles and sandwiched with carbon fiber reinforce the elastomer system. The indium tin oxide particles dispersed in the matrix allows the dissipation of static electricity throughout the structure when subjected to the ionic environment at high temperature, fine polyamide scrim helps in heat dissipation and the rubber sandwiched layer enhances the flexibility in the structure (Willis and Hsieh, 2000). The same layer by layer adhesion principle is also applied to barrier-enhanced carbon fiber reinforced plastic (BECFRP) (Anguita *et al.*, 2019). In such a multi-functional composite, the reinforcing layer is allowed to diffuse within the matrix layer. The diffusion involves unique methods like etching or plasma exposure, which matches the stress on the surface of the reinforcement with the matrix. stress-matched surface reduces the stresses and contamination at the surface, resulting in stronger adhesion and mechanical integrity, even after thermal cycles. This layer was then integrated with the barrier layer through the sandwich mechanism and thus improves the strength of the material. Fig. 16 presents a cross-section of the coating after deposition on a CFRP surface that is highly structurally featured with protrusions with a radius of curvature of 1–2 μm with the typical layer by layer structure of BECFRP for the better understanding of the concept. The other major component of the satellite is its receiver and transmission disc.

The multifunctional polymeric composite also caters to the design market of airplanes, jets, and space crafts. Glass, carbon, and Kevlar fiber composites have been routinely designed and manufactured for aerospace parts. The aerospace industry primarily uses carbon fiber composites because of their excellent mechanical and thermal properties. In addition to this, such material exhibits high weight-saving properties with excellent dimensional stability. The application requires the sustainability of the material within -100 to $+100^\circ\text{C}$ (low earth orbit). To which the epoxy-PU laminate with hybrid (carbon and flax) fiber reinforcement composite complies. Table 3 express the application of multi-functional composite in the aircraft and jet parts with their multi-functional nature.

Recently, the polymeric matrix multi-functional composite was explored in the realm of ablation composite. Ablation composites are those composites which often used as the sacrificial materials. Phenolic resin/asbestos cloth/layered silicate nanocomposite also showed excellent ablation properties. At $9 \times 10^6 \text{ W/m}^2$ external heat flux and 3400K temperature of hot gas conditions, the effective thermal diffusivity of resol type phenolic resin-asbestos cloth composite and montmorillonite layered silicate nanocomposites. The composite shows the formation of the sacrificial layer of resol when subjected to the high heat flux (Fig. 17).

Table 3 Multi-functional composite used in the aircraft and jet parts

Sr. No	Matrix phase	Reinforcement phase	Application	Properties	References
	PVDF modified Epoxy	Short glass fiber	VOR antenna	● EMI shielding ● Excellent dimensional stability ● Good deflection properties	(Mahdavi, 2017)
2	Epoxy	Phenolic coated aramid fiber paper, Carbon Fiber	S-Ducts	● high strength to weight ratio ● Excellent resilience ● Insulation properties	(Ghori <i>et al.</i> , 2018)
3	Comingled thermoplastic Or ABS	Carbon fiber and graphene	Main landing gear	● Excellent tribological properties ● Good shock absorption	(Ghori <i>et al.</i> , 2018)
4	Bismaleimide	Polyimide honeycomb structure	Leading-edge radome	● Lightweight ● Excellent abrasion resistance ● Thermal stable at low temperature	(Fischer, 2016)
5	Epoxy/polyimide PMR – 15	Carbon/Kevlar fiber	Inlet housing	● Thermal resistance upto 400°C ● Heat dissipation properties ● Excellent cracking resistance	(Sun <i>et al.</i> , 2019a)

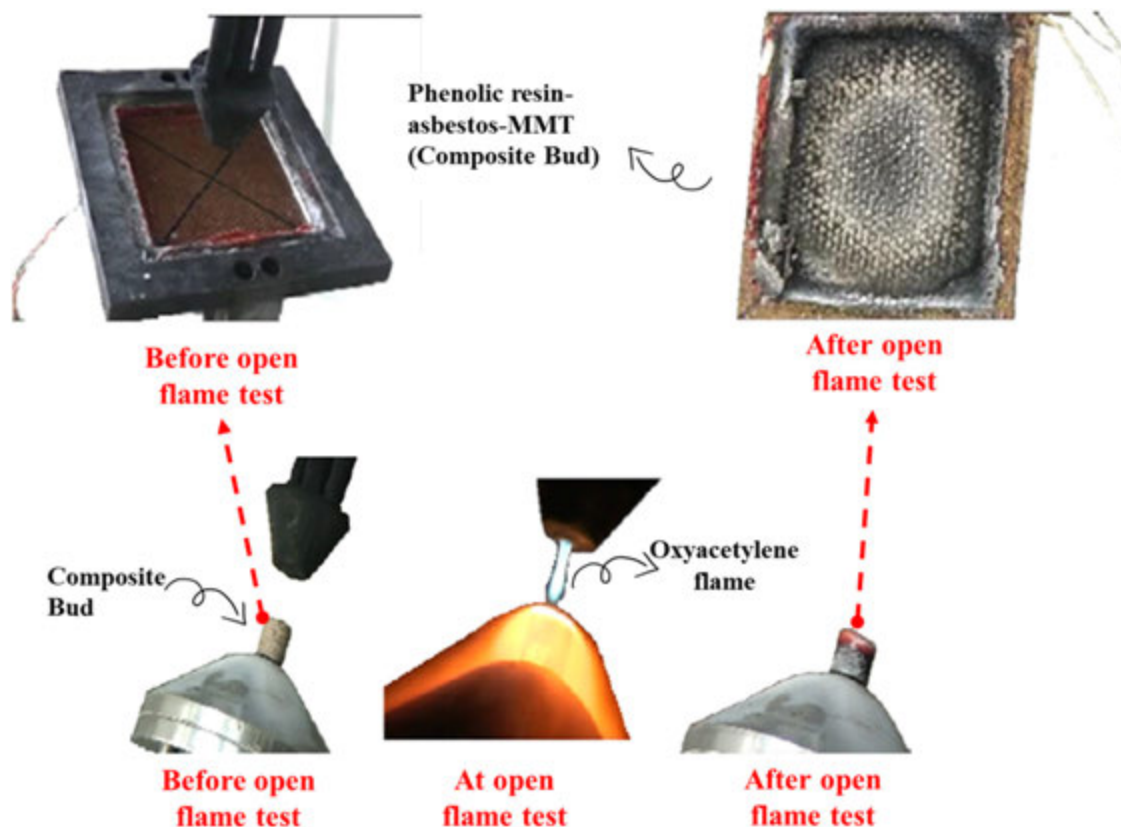


Fig. 17 Phenolic resin/asbestos cloth/layered silicate nanocomposite ablation performance under oxyacetylene flame. Reproduced from Bahramian, A.R., Kokabi, M., 2009. Ablation mechanism of polymer layered silicate nanocomposite heat shield. *Journal of Hazardous Materials* 166, 445–454. doi:10.1016/j.jhazmat.2008.11.061.

Specialty polymers like poly(phenyl silylene) and polyphenylene have excellent heat resistance and ablate at a higher temperature. Because of which the carbon fiber and glass fiber added composite of such matrix have potential use in the heat shield applications. The poly(phenyl silylene) has reactive -Si-H and -C-C- triple bond, therefore, it is cross-linked above 150°C by hydrosilylation reaction between -Si-H and -C-C- triple bond which result in limited mass loss.

Heat Exchangers

Metals and alloys like iron, steel, copper, etc. are widely used as the material of construction for different heat exchangers because of their excellent thermal conductivity and heat dissipation factor. However, they are prone to fouling and corrosion because of which such structure requires frequent maintenance and changing of assemblies. To resolve this issue, polymeric matrix composite is widely considered because of its excellent fouling and corrosion resistance, ease of manufacturing, ability to handle liquid and gases and weight, space, and volume savings.

Composite of linear low-density polyethylene (LLDPE) filled with aluminum nitride particle shows thermal conductivity three times higher than the pure LLDPE. The aluminum nitride particle dispersed in the LLDPE facilitates the localization of heat absorption and then dissipates the heat throughout the composite structure. In contrast, the LLDPE matrix allows the incorporation of flexibility and hinge-ability in the composite structure. Hence, for such composite, the concentration of the aluminum nitride is the key entity to fine-tune the thermal conductivity. To further increase the heat exchange properties of the system, polyphenylene sulfide filled with spherical hexagonal boron nickel. PPS matrix exhibits excellent resistance to acid attack. It has not been found to dissolve in any solvent at temperatures below about 200°C , because of which it is widely used for such chemical unit operation where the heat exchanging fluid is corrosive in nature (Leung *et al.*, 2013).

Recently, vapor grown carbon fiber (VGCF) base polymeric matrix composite is of significant interest in heat exchange application. The addition of VGCF in the epoxy matrix enhances the thermal conductivity of the composite and allows the use of such composite for electrical heat exchanging devices (Chen and Ting, 2002). The carbon nanoparticle filled polylactic acid (PLA), and polyamide 12 (PA 12) base matrix composites were selected as replacement of copper absorbers. The PA 12 and PLA matrix have excellent mechanical strength and flexible in nature, whereas the addition of 5% carbon nanotubes in the polymeric matrix with carbon fiber enhances the thermal conductivity by 25% in the composite. To reduce the thickness of such multi-functional composite, the coating routes are widely explored, it comprises of the coating of the multi-functional composite on to the metal substrate or inside the metallic tubes used for heat exchanging operation.

The coating route facilitates the use of thermal conductivity of the metal and the inner composite coating prevents the fouling and corrosion of the tube. The coating of nickel-copper-phosphorus-polytetrafluoroethylene (Ni-Cu-P-PTFE) composite coatings on stainless steel substrates are some typical examples. Ni-Cu-P-PTFE composite coatings imply excellent hydrophobic nature. The PTFE matrix prevents the fouling and cavitation inside the tube when delivered with salt water, and the addition of copper to the Ni-P moiety is found to improve the corrosion resistance of the coatings. Polymeric hollow fibers base composite are also widely used in the heat exchanger films and panels. The polymeric hollow fibers incorporated in the PEEK matrix for surface heat exchanging in the fins. The plate heat exchanger has the PEEK film sandwiched between two metallic frames and reinforced with hollow fibers of PE or UHMWPE. The hollow fibers entrap the air in the hollow moiety and increase the heat transmission efficiency of the heat exchanger (Christmann *et al.*, 2013).

Others

Pressure vessels and chemical reactors

The fundamental criteria required in selecting the materials for chemical reactors and vessels are: (1) chemical inertness in the material (2) excellent mechanical strength, (3) excellent thermal resistance, and (4) excellent resistance toward crack propagation. All of such properties are difficult to acquire in the single material. Thus multi-functional composites are considered to be an excellent option for construction materials for pressure vessels and chemical reactors. For example, the use of silane-modified epoxy/ carbon fiber composite in the construction of the cylindrical pressure vessel. The long carbon fiber was matted in the single yarn and then dipped in the modified epoxy resin before forming over the cylindrical core. The epoxy-coated carbon fiber yarn was wound over the cylindrical pattern at 15° longitudinal tows in the first step, and then the winding is done at 90° hoop tow. Because of the overlapping of the winding, the composite creates an excellent intact structure, and thus the thermal and mechanical stresses get uniformly distributed throughout the structure. As a result, the cylinder or reactor can sustain a high-pressure reaction (Shao *et al.*, 2016).

For many hydrogen containment vessels, the fiber wound composite of high-density polyethylene (HDPE) and glass fiber dipped in unsaturated polyester are widely used. The HDPE/silica is used as a material of construction of the liner. The compounded composite of HDPE and silica was molded into the desired shape of the liner through rotational molding. After the continuous glass fibers, yarn dipped in UPR was wound over the HDPE liner. The winding is done over the 15° longitudinal tows and then at 90° hoop tow (Nunes *et al.*, 2010). The HDPE liner provides dimensional stability in the structure and contains the hydrogen to prevent its direct contact with the UPR-glass fiber. Whereas the glass fiber helps in the enhancement of the thermal resistance of the structure, and the binder (UPR) will distribute the mechanical force in all directions and thus increase the bursting strength of the vessel.

In industries, many of such applications are presents which demand the storage of the low-temperature liquid or need cryogenic storage tank or vessels. For such an application, the composite of PEEK and nylon fiber/carbon fiber hybrid composites were considered. PEEK matrix has the capability of containing corrosive liquid at low temperature without any swelling of liquid or gas migration. Due to which the liner of such vessels was produced with PEEK material added with talc nanoparticles. Talc nanoparticles occupy the interstitial sites of the PEEK matrix and enhance the migration resistance of the composite.

Petroleum pipes

Fiber-based polymeric composites are widely used in the pipes used for the transportation of oil and natural gases. Mainly the glass fiber and carbon fiber reinforcement are widely used in such pipes with thermoplastic and thermosetting matrix. GFRP pipes have a high strength to weight ratio. They are considerably lighter than steel or concrete pipes of comparative strength and also exhibit excellent resistance to abrasion. Due to which the glass fiber reinforcement is more popular than that of the carbon fiber reinforcement. For lubricant transportation, the short glass fibers were incorporated within the HDPE and PP matrix and drawn in the hollow pipe by extrusion. In such a composite, the HDPE/PP matrix will resist the oil swelling in the material, and the glass fiber reinforcement allows the pipe to bear internal and external pressure without deformation. Inorganic filler materials, such as hydrated alumina, glass microspheres, clay, talc, calcium carbonate, calcium silicate, and sand, are sometimes used to increase the economic benefit and performance of GFRP pipes. But when the liquid is volatile and of low viscosity, in the condition, the hydrothermal cracking and aging in the pipe should be considered during its designing. In respect to this the epoxy and vinyl ester-based glass fiber composite pipes are deployed for transporting petroleum oil. Reinforced thermoplastic pipes are flexible and spoolable in nature, where the reinforcement continuously wound onto the thermoplastic liner. Liners currently PE, but could be PA12 or PVDF. Reinforcement is aramid, PET, or wire, usually encapsulated in a PE tape to aid application, but not impregnated. Tape may or may not be bonded to the liner. Glass or carbon reinforcement not used, as the perception is that these cannot be used in the unwetted state.

Steel pipeline repairs

Steel pipelines are widely used in convey hot liquid from one point to another point in the chemical industry. The adverse condition of temperature and pressure in the pipe leading to the development of cracks, leaks, and ruptures. At the same time, when the corrosive liquid is the transporting liquid, than the life span of the steel pipe found to be reduced. The multi-functional polymer composite can sustain such adverse conditions of pressure, temperature, and corrosion, thus suitable for such repairs. Such a pipe can be repaired with the help of different methods like – pre-cured layered system, stand-off sleeves, and infills. The pre-cured layered system involves the bonding of pre-cured fiber-reinforced composite materials that are held together with an adhesive applied—for example, the use of carbon fiber-based ultra-high temperature resistance epoxy matrix. The precured sheet of such composite was deployed over the ruptured surface and allowed to adhere to the steel. After that, a cross-layer of the composite was applied on the same layer and then allowed to cure. Aramid fiber-based composites are strongly advisable as an option of pipe rehabilitation to those areas, where the pipes are continuously exposed to the corrosive chemical. The repair heat shrink sleeve of the PE/PP matrix reinforced with thermally treated aramid fiber is widely used in the hydrodesulfurization (HSDU) plant of the petroleum industries. The petroleum refineries chemical process requires the transportation liquid and gases through pipe at elevated temperature and at such aggravate condition of temperature, the pipe inner lining becomes susceptible for cavitation and corrosion. The repair of such pipe or section of such pipe were done with the help of clay dispersed polyurethane-Kevlar fiber composite.

Multifunctional Polymeric Matrix Composite With Electrical Application

Electric energy storage system (ESS) is one of the most popular and reliable ways to store electric energy from intermittent renewable sources to ensure timely and reliable delivery of an adequate amount of electric power for portable electronic devices, electric-powered vehicles, and other applications. The electric energy storage devices comprise electrochemical batteries, solar cells, photovoltaic assemblies, and piezoelectric structures. All of these entities require durable, lightweight, functional, and high-performance base material, and thus recently, the demand for polymeric composite in such area is increasing day by day. Nowadays, such multi-functional composite is emerging, which can give a full proof solution as the material of construction for electrode, electrolyte, capacitance, and current collector in the electrochemical devices. Such advancement in the material and design increases the efficiency of the electrical storage technologies and helps in the betterment of the society.

Lithium-Ion Batteries Electrodes

Batteries are an essential class of electrochemical energy storage devices, especially lithium-ion batteries. They are prevalent rechargeable batteries and thus widely for supply power to mobile phones, laptops, electronic devices, and other portable systems like vehicles, motion communication devices, and remote location transmitting signals. The Li-ion batteries express fast charging, low density, high energy density, and low self-discharge rates but many times susceptible to leakage, rigid with their geometry, and can cause hazards. Thus, to improve the drawback of these batteries, the use of polymeric composite instead of conventional material has drawn significant research interest. Batteries comprise anode, cathode, and electrolytes, this section projects the use of

Table 4 PANI-carbon nanotube composite – Capacitance, cycle life, and properties data

Sr. No	Composite electrode	Capacitance (F/g)	Electrolyte	Cycle life	Properties
1	PANI-MWCNT (60/40) + 15% acetylene black (15 wt%) and 5% polytetrafluoroethylene	328	1 M NaNO ₃	1000	● Excellent corrosion resistance ● Dimensional stable ● Low pitting electrode
2	73% PANI reinforced with 25% PVDF modified carbon nanotube	463	1 M H ₂ SO ₄	1000	● Low volumetric expansion ● Lightweight ● Excellent charge conduction
3	52% PANI + 38% multiwall nanotube + 6% carboxy-methyl cellulose (6 wt%) and styrene-butadiene rubber (4 wt%)	606	1 M H ₂ SO ₄	200	● Low volumetric expansion ● Excellent erosion resistance
4	80% PANI + 2% carbon black + 12% graphene	574	5–6 M KOH	600	● Self-lubricating ● Excellent charge conduction

Note: Gajendran, P., Saraswathi, R., 2008. Polyaniline-carbon nanotube composites. *Pure Applied Chemistry* 80 (11), 2377–2395. doi:10.1351/pac200880112377.

multi-functional composite in all of the constituent of the batteries. The electrode -anode and cathode construction material requires excellent corrosion resistance, mechanical strength and excellent electrical conductivity in the materials. Generally, graphite, tin and silicon alloys are widely used for the construction of the anode. All of these anode binders have excellent conductive properties. Still, because of the lithiation, the anode undergoes volumetric expansion and thus the limit the use of such batteries.

The polymer with highly conjugated chains allows the motion of electron with the structure and thus causes the flow of current through the lattice. Such polymers are called as a conductive polymer, the examples of such polymer are polyacetylene (PA), polypyrrole (PPy), polythiophene (PTh), poly(*p*-phenylenevinylene) (PPV), polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT). The incorporation of carbon nanotube into the PANI matrix is expected to enhance its electrical and mechanical properties, which are essential for actual device fabrication. Table 4 indicates the capacitance (storage ability), the life cycle of the PANI-carbon nanotube-based composite electrode used for different electrolytic batteries.

PANI-carbon nanotube composites can be used as efficient electrocatalytic materials in fuel cell reactions like oxygen reduction and methanol oxidation. The CNT provides higher surface area and better electronic conductivity while PANI facilitates the electron transfer through the conducting matrix. The dispersion of graphene oxide, reduced graphene oxide, and graphite nanoflakes based reinforcements in the polyaniline matrix have attracted considerable interest in the fields of electrochemical energy storage application, and such composite base electrodes are called as polyaniline-2D carbon composite electrode. The typical example is polyaniline (PANI)-graphene sheet (GO) and reduced graphene oxide (rGO) composite added with carbon nanotube (CNT) and MnO₂ particles to increase the capacitance value. Fig. 18 compares the specific capacitance of such composites. It was observed that the reduced graphene oxide has better specific capacitance value as compared to the graphene sheets (Sathish *et al.*, 2011).

The composite of V₂O₅ nanobelt arrays (NBAs) was directly grown on 3D ultrathin graphite foam (UGF) as shown in, and then subsequently coated by a mesoporous thin layer of the conducting polymer of PEDOT (Chao *et al.*, 2014). PEDOT based metal oxides/hydroxides hybridized composite provide the most promising performance with reduced cost and weight. For example, RuO₂/PEDOT nanotubes with a high specific capacitance of 1217 F/g and a high power density of 20 kW/kg from the high specific surface area and fast charge/discharge of the tubular structures.

The non-conductive polymer composite for electrode application follows the compounding route, where the non-conductive polymeric matrix is incorporated with conductive moieties. Such composites have easy to process nature with excellent functional properties. Electrode binders like polyvinyl alcohol (PVA), Carboxymethyl cellulose (CMC), Styrene-butadiene rubber (SBR) are widely preferred for the construction of the electrode. The binders were added with conductive reinforcement like carbon black, graphite, graphene, Carbon nanotubes, and collectors such as aluminum, nickel, Ag, Au, Pt, alloys, graphene for cathode and copper, nickel for the anode to prepare a multi-functional composite. For example, the composite of styrene-ethylene-butylene-styrene (SEBS) reinforced with HDPE added carbon fiber had been shown excellent electrical and mechanical properties. The styrene base polymer causes ease of processability and makes it suitable for electrode application. The butylene-styrene component of the matrix restricts the volumetric expansion of the anode. Whereas, the presence of carbon nanotube in the HDPE fiber impart electrical conductivity in the composite and make it suitable for higher capacity batteries.

Another example is the use of eco-friendly and low-cost cellulose. For example, the composite of carboxyl methylcellulose (CMC) and polyvinyl alcohol (PVA) with graphene nanospheres added with aluminum oxide. The ability of CMC and PVA to swell in liquid

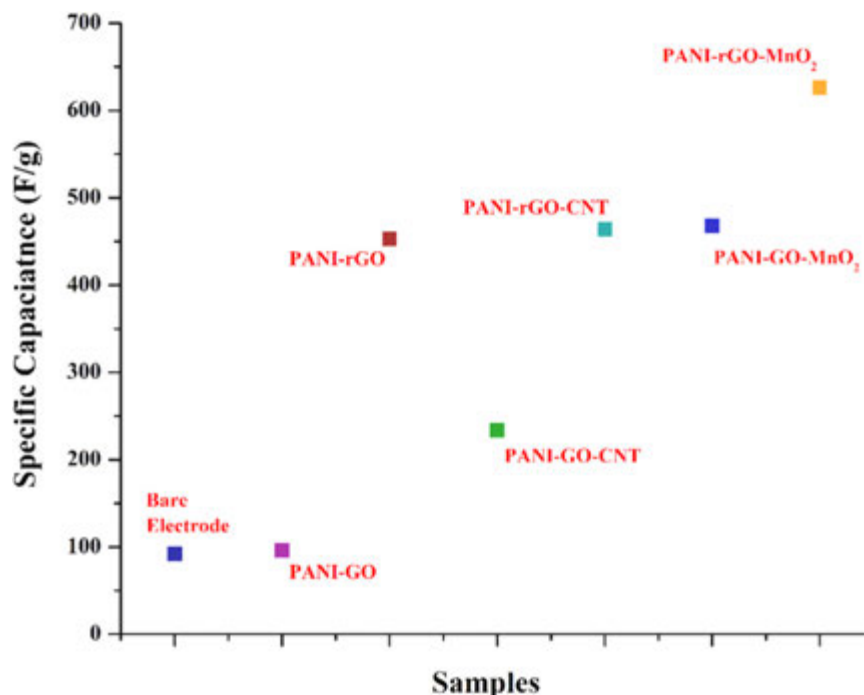


Fig. 18 Effect of addition of capacitive reinforcement like CNT and MnO₂ in the PANI-graphene matrix on their specific capacitance values.

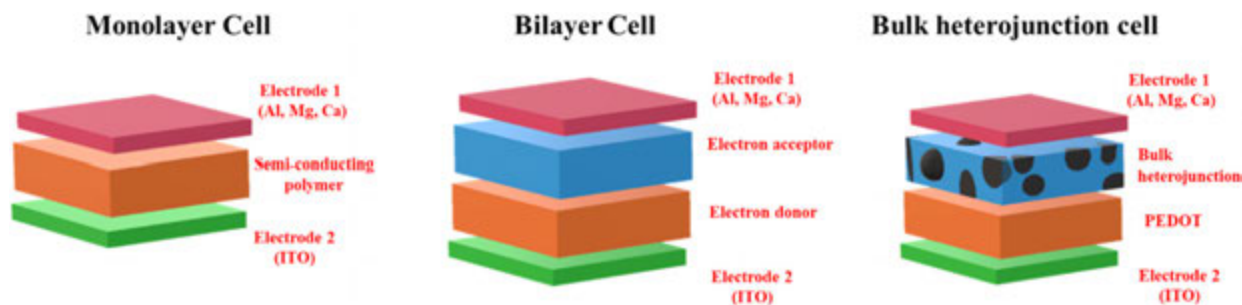


Fig. 19 Nature and structure of monolayer, bilayer, and bulk heterojunction composite system and location of polymeric matrix composite layer in the solar cell.

electrolytes influenced the electrical properties of graphite electrodes. The CMC allows the bridging between electrolyte and electrode component and impart excellent charging and discharging capabilities for higher cycles (Nirmale *et al.*, 2017).

Solar Cells

Photovoltaic cells have recently gained tremendous attention as the replacement of the conventional silicon-based solar cells. Most of the photovoltaic cells have organic constituents because of which they are flexible, easy to process, and efficient. Although, a single polymeric system of such cells has instability under the exposure of oxygen, UV light, and humidity. Thus, multi-functional composite material such as an indium-doped tin oxide (ITO)/polyethylene naphthalate (PEN), which have excellent UV and oxygen resistance, were widely used in modern solar cells.

Fig. 19 shows the nature of the first three types of composite systems and the location of the polymeric matrix composite layer in the solar cell.

The monolayer solar cell comprises the polymeric composite of semi-conductive nature. Generally, poly(ethyleneimine) (PEI) and poly-(ethyleneimine)-ethoxylated (PEIE) matrix were used for the preparation of such composite. To increase the semi-conducting behavior, the polymer matrix was intensively doped with ZnO-graphene core-shell type quantum dots. The quantum dots play a multi-functional role as surface modifier, sub-photosensitizer, and electron transport layer. The transport layer shifts the charge to zinc oxide particle and then carries forward the charge to the graphene sheet. This path and rapid jumping of the

Table 5 Effect of nature and treatment of CNT in P3HT matrix on the open voltage of the solar cell

Sr. No	Nature of CNT	Treatment on CNT	Additive system	Matrix phase	Dose of CNT (%)	Open circuit voltage (mV)
1	MWCNT	Acid treatment – H ₂ SO ₄ and HNO ₃	PCBM	P3HT	1	570
2	MWCNT	Octyldecylamine	PCBM	P3HT	1	560
3	MWCNT	Carboxylated and sulfonated	C60	P3HT	1	386
4	DWCNT	75% HCl treatment	PCBM	P3HT + BDQF	1	530
5	SWCNT	Acid treatment, SDS treatment	–	P3HT	1	750
6	SWCNT	Acid treatment – H ₂ SO ₄ and HNO ₃	PCBM	P3HT	1	540
7	SWCNT	Non-covalent functionalization with the polymer	–	P3HT	1	580

Abbreviation: PCMB, (6,6)-phenyl-C61-butyric-acid methyl ester; BDQF, 2,7-Bis-(3,3''didodecyl-[2,2',5',2'',5'',2'''] quaterthiophen-5-yl))-fluoren-9-one; SDS, Sodium dodecyl sulfate.

charge increase the efficiency of the chain. Similarly, the thin nanocomposite film of poly(9,9-di-*n*-octylfluorenyl-2,7-diyl)(F8) blended with poly(9,9-dioctylfluorene-*alt*-benzothiadiazole)(PFB) matrix reinforced with nickel and zinc oxide on to the ITO electrode shows excellent electrical semi-conduction properties. PFB capping layer effectively reduced the performance of the device due to its blocking of photogenerated electrons in the F8-rich phase from reaching the electrode.

The modification of F8 and PFB with different layers encourages the concept of the bilayer polymer composite where the one phase will be the donor phase, and others will be the acceptor phase. The use of bi-layers structure decreases the recombination probability of the carriers because the free charge carriers migrate in their respective domains towards the electrodes. In such composite PFB layer is commonly used as the donor and F8BT (poly(9,9'-dioctylfluor-ene-*co*-benzothiadiazole)) as the electron acceptor (Borges *et al.*, 2018).

Polymer-polymer composite solar cells can be constructed using a phenyl octyl-substituted polythiophene derivative with donor and acceptor layer resulted in higher efficiency under full air mass 1.5 illuminations (100 mW/cm²) (Hoppe and Serdar, 2008). Bilayer polymer composites of multi-wall carbon nanotube and poly(3-hexylthiophene) (P3HT) were also explored in the polymer-inorganic regime for solar cell application. Table 5 enlist the matrix and CNT combination with various additive systems and intent to compare the open circuit voltage of the composites. This composite helps in enhancing the thermal stability of the solar cell and imparting the excellent performance properties – the addition of multi-wall carbon nanotubes in polymer matrix increases the open-circuit voltage of the solar cell, the multi-wall structure helps in maintain the potential throughout the matrix.

The last type of polymer composite solar cell is of bulk-heterojunction (BHJ) design; these design forms the donor/acceptor interface at the molecular scale and increases the exciton dissociation sites. Higher the number of sites will improve the light-induced flow of electron and thus improve the conversion efficiency. The new example BHJ type solar cell composite is PEDOT: PSS arranged in the layer composite with gold and modified graphene nanoparticle and sandwiched between electrode layers (Rezaei *et al.*, 2019). In this, the gold nanoparticles with graphene shell (Au NPs-Gr), positioned between hole transport and active layers. The graphene shell improves the intactness of the gold particle within the bulk-heterojunction layer and thus facilitated charge transfer in the solar cell. Because of which the open-circuit voltage of the solar cell improves by 42% when compared with the conventional solar cells. Most functional polymeric composite of PANI is widely used as the heterojunction phase coupled with the PEDOT system. The bulk junction of carbon nanotubes was created in the PANI matrix, because of which the bandgap in the structure can be tuned for low light solar cells.

Piezoelectric Components

Generally, the piezoelectric effect constitutes certain behavior of polymeric material because of which they generate an electrical potential whenever exposed to mechanical stimuli. The crystalline part of the polymer produces electrical charges across the lattice boundaries or chain boundaries in response to the applied force or pressure. Polymeric matrix-like polyvinylidene fluoride (PVDF) and its copolymers, cellulose and their derivatives, polylactic acids (PLA), polyurethanes (PU), polyimides (PI) show inherent piezoelectric performance. When these polymer matrices were mixed with ceramic particles, their ability to generate charge increases. For example, the composite of polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) and ceramic barium titanate nanoparticles (BaTiO₃) with additional reinforcement of the hexagonal boron nitride (*h*-BN) nanolayers. The composite showed excellent piezoelectric output voltage (2.4 V) with high dielectric constant (45) and low dielectric loss (7.8). The PVDF phase allows the absorption of the mechanical force or pressure applied to it and transmits the force towards the localized ceramic particle. Ceramic particle exhibits ferroelectric properties because of which a higher potential was created along the boundary. This effect gets aggravated in the presence of hexagonal boron nitride. The hexagonal structure of boron nitride or white graphene possesses excellent dielectric properties with excellent mechanical strength and oxidation resistance. Because of which the addition of hexagonal boron nitride with BaTiO₃ allows the designer to tune the composite according to the application (Ponnamma and Al-maadeed, 2019).

Li₂CO₃/PVDF based composite has demonstrated improvement in the dielectric and piezoelectric properties with maintaining the flexibility of the composite. Instead of such a versatile nature, the PVDF based composite was not ideally used for high-

temperature applications. At high temperature, the phase transformation from polar β -phase to nonpolar α - and γ -phases of PVDF occur because of which the matrix loses its electromechanical properties.

Poly(γ -benzyl- α , L-glutamate) (PBLG) is one of the emerging polymer matrices which shows the piezoelectric behavior like PVDF and thermally stable at high temperature. PBLG allows the scouting of the polymer-polymer composite in the piezoelectric application. PBLG has well defined helical conformation, which causes axial orientation and thus generate polarization in the presence of shear force. Polarization in the structure draws the balance between positive and negative charge in the structure. The PMMA/PBLG composite with 30% PBLG reinforcement has durable piezoelectric behavior with excellent chemical resistance.

Polyvinyl alcohol (PVA) is a good insulating material with low conductivity, hence it is very useful in microelectronic industry. For example, barium titanate reinforced polyvinyl alcohol have shown frequency and temperature dependence dielectric behavior. Stable dielectric properties make the PVA/barium titanate polymer ceramic composites as a good candidate material for various industrial applications. PLA-based polymers are becoming a popular candidate for energy harvesting applications owing to their higher piezoelectric properties.

Others

Flexible conductors

Flexible conductor made up of polycarbonate/PMMA matrix reinforced with SOCl_2 modified SWCNT composite showed five times higher electrical conductivity as compared to the normal polymeric matrix. In such a composite, the optical transparency is dependent on the SWCNT. The higher loading of the SWCNT may drop the transparency. Although, in current literature, it was found that the addition of 0.1%–0.5% of SWCNT in the polymeric matrix shows 92% of optical transparency in the composite (Dettlaffeglikowska *et al.*, 2006). The flexible conductors were also constructed using the HDPE matrix imbedded with iron nanoparticle. The 7% acid-coated iron nanoparticle have been dispersed in the HDPE matrix in support of PANI short fibers. The iron nanoparticle with PANI fibers helps in enhancing the electrical conductivity of the composite, and chemically inert nature of the HDPE matrix allows the use of such composite in reactive sensors circuit. Where the sensors are in direct contact with the reacting liquid or compounds.

Microelectronics

Microelectronics includes the smaller design component like diodes, transducer, and resistors made up of semiconducting materials. Polymer composite light-emitting diodes and polymer light-emitting electrochemical cells have attracted broad interests due to their large potentials in serving as next-generation displays and illuminants. Composite of poly(para-phenylene) matrix with carbon fiber reinforcement have exhibit high photoluminescence (PL) in the blue color region with excellent quantum yields, charge-carrier mobility, and good processability. Poly[2,7-(9,9'-dioctylfluorene)-*alt*-1,3-(5-carbazolphenylene)] (PFCz) composite with secondary phase of zinc oxide have found wider application in UV blue-light-emitting systems. Similarly, conjugated fluorene-*alt*-pyridine and fluorene-*alt*-thiophene polymers containing phosphorescent iridium base composite shows phosphorescent quantum yield and thus have superior light-emitting. Similarly, the use of arranged CNT array in the PDMS matrix imparts anisotropic thermal conductivity, which provides an effective path for the frequency control of the optoacoustic devices used in the biomedical industry (Li *et al.*, 2020). The dropping of carbon nanotubes and ethoxyethanol on the polyethylene microsphere composites are widely used in the frequency modulation of the laser ultrasound transducer.

Solder joints

A polymer-metal composite can be used as a solder material, where polymer acts as a binder and metal power, such as silver acts as a thermal conductor. The CNT-silver base reinforcement was dispersed in epoxy-based conductive adhesives and used for soldering the joints in printing circuit boards. The resistivity of 66.5 wt% silver-filled conductive adhesive without CNT loading had $10^4 \Omega \text{ cm}$, whereas $10^4 \Omega \text{ cm}$ of resistivity was shown for adding 0.27 wt% CNT, which shows that the polymer composite adhesive can replace conventional silver metal filler. Recently the development of lead-free soldering adhesive has attracted high commercial interest. Polyimide-siloxane base composite with graphene and metal particles have established a significant market for such adhesive. The metal particle insured the distribution of heat energy. It enhanced the thermal conductivity of the adhesive, whereas the polymer matrix and graphene fill the ruptured gap and hold the component at its place.

Summary

This article provides a broad picture of the structure, properties, and application of the multifunctional polymer matrix composite. Almost every example provided within the article intends to project the degree of multifunctionality present or required for the application. The combination of different properties associated with matrix, reinforcement, and structural diversity of multifunctional composite helps in designing new material which has tremendous application the filed construction, automobile, mechanical devices, sensors, packaging safety devices, solar cells, and energy-conserving devices. In many cases, the strength of material and density are the factors for design consideration, whereas, in other stimuli response, thermal stability and conductive properties are of main interest. In some example, the multi-functionality is the matrix-based response. In contrast, other examples

may show reinforcing component base multifunctionality in the case of structural application, the design and structure of composite play a vital role. The design and the interaction of the matrix and fiber in layer or dispersed form decide the degree of multifunctionality and suitability of polymer matrix composites. For stimuli-responsive application, the chemistry of matrix and reinforcement have higher importance than that of its structure. The chemical functionality in the composite decides the multiple responses of the composite against single or multiple stimuli. In the case of high-temperature applications, the chemistry, morphology, and thermal properties are the points of considerations with other functional properties like density and processability of the composites. Similarly, the composites in batteries, solar cells, and electronics applications require such polymeric matrix composite, that can constitute excellent electrical properties with chemical inertness and mechanical stability. All of such modern application requires the combination of different properties which multi-functional polymeric composite can easily serve.

References

- Agronin, M.L., 2000. Method and Apparatus for Providing Erasable Relief Images. US006092465A, pp.1–24.
- Aly-Hassan, M.S., 2015. Chapter 2 – A new perspective in multifunctional composite materials. In: Friedrich, K., Breuer, U. (Eds.), *Multifunctionality of Polymer Composites*. Elsevier, pp. 42–67.
- Anguita, J.V., Smith, C.T., Stute, T., *et al.*, 2019. Polymer composites reinforced with carbon fibres. *Nature Materials* 19 (1), 317–322. doi:10.1038/s41563-019-0565-3.
- Biji, K.B., Ravishankar, C.N., Mohan, C.O., 2015. Smart packaging systems for food applications: A review. *Journal of Food Science and Technology* 52, 6125–6135. doi:10.1007/s13197-015-1766-7.
- Borges, B.G., Veiga, A.G., Gioti, M., *et al.*, 2018. Surface, interface and electronic properties of F8: F8BT polymeric thin films used for organic light-emitting diode applications. *Polymer International* 67, 691–699. doi:10.1002/pi.5552.
- Chao, D., Xia, X., Liu, J., *et al.*, 2014. A V_2O_5 /conductive-polymer core / shell nanobelt array on three-dimensional graphite foam: A high-rate, ultrastable, and freestanding cathode for lithium-ion batteries. *Advanced Materials* 26 (33), 1–7. doi:10.1002/adma.201400719.
- Chen, H., Gao, Z., Cui, Y., Chen, G., Tang, D., 2013. Nanogold-enhanced graphene nanosheets as multienzyme assembly for sensitive detection of low-abundance proteins. *Biosensors and Bioelectronics* 44, 108–114. doi:10.1016/j.bios.2012.12.054.
- Chen, Y., Ting, J., 2002. Ultra high thermal conductivity polymer composites'. *Carbon* 40, 359–362. doi:10.1016/S0008-6223(01)00112-9.
- Christmann, J.P., Krätz, L.J., Bart, H., 2013. Falling film evaporation with polymeric heat transfer surfaces. *Desalination* 308, 56–62. doi:10.1016/j.desal.2011.05.027.
- Correia, C.O., Alvaro, J., Leite, J., Mano, F., 2015. Chitosan/bioactive glass nanoparticles scaffolds with shape memory properties. In: Kennedy, J.F., Coimbra, M. (Eds.), *Carbohydrate Polymers*, vol. 2. Elsevier, pp. 1–24. doi:10.1016/j.carbpol.2014.12.076.
- Detlaffeglikowska, U., Kaempgen, M., Hornbostel, B., 2006. Conducting and transparent SWNT/polymer composites. *Physica Status Solidi* 243 (13), 3440–3444. doi:10.1002/pssb.200669188.
- Eisenhaure, J., Kim, S., 2014. An internally heated shape memory polymer dry adhesive. *Polymers* 6, 2274–2286. doi:10.3390/polym6082274.
- Fam, A., Sharaf, T., 2010. Flexural performance of sandwich panels comprising polyurethane core and GFRP skins and ribs of various configurations. *Composite Structures* 92 (12), 2927–2935. doi:10.1016/j.compstruct.2010.05.004.
- Fischer, G., 2016. High Temperature and Toughened Bismaleimide Composite Materials for Aeronautics. vol. 14. Université De Lyon. pp. 10–57.
- Ghori, S.W., Siakeng, R., Rasheed, M., Saba, N., Jawaid, M., 2018. Chapter 2 – The role of advanced polymer materials in aerospace, sustainable composites for aerospace applications. In: Jawaid, M., Thariq, M. (Eds.), *Sustainable Composites for Aerospace Applications*. Elsevier, pp. 19–34. doi:10.1016/B978-0-08-102131-6.00002-5.
- Gök, M.O., Bilir, M.Z., Gürcüm, B.H., 2015. Shape-memory applications in textile design. *Procedia - Social and Behavioral Sciences* 195, 2160–2169. doi:10.1016/j.sbspro.2015.06.283.
- Han, E., Dan, S., Huaiguo, X., Serge, C., 2007. Hybrid material based on chitosan and layered double hydroxides: Characterization and application to the design of amperometric phenol biosensor. *Biomacromolecules* 8, 971–975. doi:10.1021/bm060897d.
- Holschuh, B., Newman, D., Obropta, E., 2015. Controllable Compression Garments Using Shape Memory Alloys and Associated Techniques and Structures. US 2015/0073318A1. pp. 1–24.
- Hoppe, H., Serdar, N., 2008. Polymer solar cells. *Advance Polymer Science* 214, 1–86. doi:10.1007/12_2007_121.
- Kalra, S., Munjal, B.S., Singh, V.R., Mahajan, M., Bhattacharya, B., 2019. Investigations on the suitability of PEEK material under space environment conditions and its application in a parabolic space antenna. *Advances in Space Research* 63 (12), 4039–4045. doi:10.1016/j.asr.2019.03.006.
- Keller, T., Vassilopoulos, A.P., Manshadi, B.D., 2010. Thermomechanical behavior of multifunctional grfp sandwich structures with encapsulated photovoltaic cells. *Journal of Composites for Construction* 4 (1), 470–478. doi:10.1061/ASCECC.1943-5614.0000101.
- Khun, N.W., Sun, D.W., Huang, M.X., Yang, J.L., Yue, C.Y., 2014. Wear resistant epoxy composites with diisocyanate-based self-healing functionality. *Wear* 313 (1–2), 19–28. doi:10.1016/j.wear.2014.02.011.
- Leung, S.N., Khan, M.O., Chan, E., *et al.*, 2013. Analytical modeling and characterization of heat transfer in thermally conductive polymer composites filled with spherical particulates. *Composites Part B* 45 (1), 43–49. doi:10.1016/j.compositesb.2012.10.001.
- Li, J., Xu, J., Liu, X., *et al.*, 2020. A novel CNTs array-PDMS composite with anisotropic thermal conductivity for optoacoustic transducer applications. *Composites Part B* 196, 108073. doi:10.1016/j.compositesb.2020.108073.
- Liu, X., Yang, Q.S., Liew, K.M., He, X.Q., 2017. Superstretchability and stability of helical structures of carbon nanotube/polymer composite fibers: coarse-grained molecular dynamics modeling and simulation. *Carbon* 115, 220–228. doi:10.1016/j.carbon.2017.01.007.
- Liu, Y., Zwingmann, B., Schlaich, M., 2015. Carbon fiber reinforced polymer for cable structures – A review. *Polymer* 7 (10), 2078–2099. doi:10.3390/polym7101501.
- Mahdavi, S., 2017. Thermal Cycling of Out-of-Autoclave Thermosetting Composite Materials. Quebec: Concordia University Montreal.
- Muschenborn, A.D., Hearon, K., Volk, B.L., Conway, J.W., Maitland, D.J., 2014. Feasibility of crosslinked acrylic shape memory polymer for a thrombectomy device. *Smart Materials Research* 2014, 1–12. doi:10.1155/2014/971087.
- Nguyen, H., Mutsuyoshi, H., Zatar, W., 2014. Push-out tests for shear connections between UHPFRC slabs and FRP girder. *Composite Structure* 118, 528–547. doi:10.1016/j.compstruct.2014.08.003.
- Nirmale, T.C., Kale, B.B., Varma, A.J., 2017. A review on cellulose and lignin based binders and electrodes: Small steps towards a sustainable lithium ion battery. *International Journal of Biological Macromolecules* 103, 1032–1043. doi:10.1016/j.ijbiomac.2017.05.155.
- Nunes, J., Silva, J.V., Marques, A., 2010. Fibre reinforced thermosetting and thermoplastic matrix filament wound pressure vessels. *ASME Pressure Vessels and Piping Conference* 6 (1), 1–12. doi:10.1115/pvp2010-25826.
- Ortega, J.M., Small, W., Wilson, T.S., *et al.*, 2007. A shape memory polymer dialysis needle adapter for the reduction of hemodynamic stress within arteriovenous grafts. *IEEE Transactions on Biomedical Engineering* 54 (9), 1722–1724. doi:10.1109/tbme.2007.892927.
- Ponnamma, D., Al-maadeed, M.A., 2019. Influence of BaTiO₃/ white graphene filler synergy on the energy harvesting performance of piezoelectric polymer nanocomposite. *Sustainable Energy & Fuels* 3, 774–785. doi:10.1039/c8se00519b.

- Rezaei, B., Taromi, F.A., Ahmadi, Z., Rigi, S.A., Yousefi, N., 2019. Enhancement of power conversion efficiency of bulk heterojunction polymer solar cells using core/shell, Au/graphene plasmonic nanostructure. *Materials Chemistry and Physics* 228, 325–335. doi:10.1016/j.matchemphys.2019.02.084.
- Rouhi, M., Lakouraj, M.M., Baghayeri, M., 2016. Novel conductive magnetic nanocomposite based on poly(indole-co-thiophene) as a hemoglobin diagnostic biosensor: Synthesis, characterization and physical properties. *International Journal of Polymeric Materials and Polymeric Biomaterials* 66 (1), 12–19. doi:10.1080/00914037.2016.1180615.
- Santo, L., Quadrini, F., Accettura, A., Villadei, W., 2014. Shape memory composites for self-deployable structures in aerospace applications. *Procedia Engineering* 88, 42–47. doi:10.1016/j.proeng.2014.11.124.
- Sathish, M., Mitani, S., Tomai, T., Honma, I., 2011. MnO₂ assisted oxidative polymerization of aniline on graphene sheets: Superior nanocomposite electrodes for electrochemical supercapacitors. *Journal of Materials Chemistry* 21 (40), 16216. doi:10.1039/c1jm12946e.
- Shao, Y., Betti, A., Carvelli, V., *et al.*, 2016. High pressure strength of carbon fibre reinforced vinylester and epoxy vessels. *Composite Structure* 140, 147–156. doi:10.1016/j.compstruct.2015.12.053.
- Stratford, T., 2012. The condition of the aberfeldy footbridge after 20 years of service. *Structural Faults and Repair* 1 (1), 1–12.
- Sun, B.G., Lei, Q., Guo, Y., *et al.*, 2019a. Enhanced mechanical properties at 400°C of carbon fabric reinforced phthalonitrile composites by high temperature postcure. *Composites Part B* 166, 681–687. doi:10.1016/j.compositesb.2019.02.066.
- Suzuki, M., Wilkie, C.A., 1995. The thermal degradation of acrylonitrile-butadiene-styrene terpolymer grafted with methacrylic acid. *Polymer Degradation and Stability* 47 (2), 223–228. doi:10.1016/0141-3910(94)00113-M.
- Tassanawat, S., Phandee, A., Magaraphan, R., Nithitanakul, M., Manuspiya, H., 2007. pH-sensitive pp/clay nanocomposites for beverage smart packaging. In: *Proceedings of the IEEE International Conference on Nano/Micro Engineered and Molecular Systems*, vol. 662. pp. 478–482. doi:10.1109/nems.2007.352062.
- Vimalanandan, A., Lv, L.P., Tran, T.H., *et al.*, 2013. Redox-responsive self-healing for corrosion protection. *Advanced Materials* 25 (48), 6980–6984. doi:10.1002/adma.201302989.
- Wang, D., Zhou, K., Yang, W., *et al.*, 2013. Surface modification of graphene with layered molybdenum disulfide and their synergistic reinforcement on reducing fire hazards of epoxy resins. *Industrial & Engineering Chemistry Research* 52 (50), 17882–17890. doi:10.1021/ie402441g.
- Wang, J., Musameh, M., 2003. Carbon nanotube/teflon composite electrochemical sensors and biosensors. *Analytical Chemistry* 75 (9), 2075–2207. doi:10.1021/ac030007+.
- Wang, Z., Situ, W., Li, X., *et al.*, 2017. Novel shape stabilized phase change material based on epoxy matrix with ultrahigh cycle life for thermal energy storage. *Applied Thermal Engineering* 123, 1006–1012. doi:10.1016/j.applthermaleng.2017.05.179.
- Willis, P.B., Hsieh, C., 2000. Space applications of polymeric materials. *Kobunshi* 49 (1), 52–56. doi:10.1295/kobunshi.49.52.
- Wilson, J., Radhakrishnan, S., Sumathi, C., Dharuman, V., 2012. Polypyrrole – polyaniline – Au (PPy – PANi – Au) nano composite films for label-free electrochemical DNA sensing. *Sensors & Actuators:B* 171–172, 216–222. doi:10.1016/j.snb.2012.03.019.
- Zhu, J., Start, P., Mauritz, K.A., Wilkie, C.A., 2002. Silicon-methoxide-modified clays and their polystyrene nanocomposites. *Journal of Polymer Science Part A: Polymer Chemistry* 40 (10), 1498–1503. doi:10.1002/pola.10231.

Further Reading

- Sun, Z., Zhang, Y., Shao, H., He, A., 2019b. In situ reactive compatibilization of polypropylene/trans-1,4-poly(isoprene-co-butadiene) rubber (TBIR) blends with balanced toughness and stiffness via dynamic vulcanization. *Reactive and Functional Polymers* 142 (5), 60–68. doi:10.1016/j.reactfunctpolym.2019.06.001.